



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C08F 8/00, 8/14, B65D 65/38, C08K 5/09		A2	(11) International Publication Number: WO 95/02616 (43) International Publication Date: 26 January 1995 (26.01.95)
(21) International Application Number: PCT/US94/07854 (22) International Filing Date: 13 July 1994 (13.07.94) (30) Priority Data: 08/091,120 13 July 1993 (13.07.93) US		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KE, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
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<div style="border: 1px solid black; padding: 2px; display: inline-block;">REFERENCE COPY</div> <div style="margin-top: 5px; font-size: small;">PCT/US99/06379</div>			

Serial No. 10/684,259

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1 **ETHYLENIC OXYGEN SCAVENGING COMPOSITIONS AND PROCESS FOR**
2 **MAKING SAME BY ESTERIFICATION OR TRANSESTERIFICATION IN A**
3 **REACTIVE EXTRUDER**

4 **FIELD OF THE INVENTION**

5 This invention provides ethylenic compositions and articles. Also included are
6 compositions and methods for scavenging oxygen from environments containing
7 oxygen, particularly food and beverage-containing products. In addition, a process is
8 disclosed for transesterifying a polymer having a polyethylenic backbone and pendant
9 ester moieties in a reactive extruder to obtain a polymer having a polyethylenic
10 backbone and pendant ester moieties which differ in kind and/or in number from the
11 unreacted polymer.

12 **BACKGROUND**

13 It is well known that regulating the exposure of oxygen-sensitive products to oxygen
14 maintains and enhances the quality and "shelf-life" of the product. For instance, by
15 limiting the oxygen exposure of oxygen sensitive food products in a packaging
16 system, the quality of the food product is maintained, and food spoilage is avoided.
17 In addition, such packaging also keeps the product in inventory longer, thereby
18 reducing costs incurred from waste and having to restock inventory. In the food
19 packaging industry, several means for regulating oxygen exposure have already been
20 developed. These means include modified atmosphere packaging (MAP) and oxygen
21 barrier film packaging.

22 One method currently being used is through "active packaging", whereby the package
23 for the food product is modified in some manner to regulate the food product's
24 exposure to oxygen. The inclusion of oxygen scavengers within the cavity of the
25 package is one form of active packaging. Typically, such oxygen scavengers are in
26 the form of sachets which contain a composition which scavenges the oxygen through

1 oxidation reactions. One sachet contains iron-based compositions which oxidize to
2 their ferric states. Another type of sachet contains unsaturated fatty acid salts on a
3 particulate adsorbent. See U.S. Patent No. 4,908,151. Yet another sachet contains
4 metal/polyamide complex. See U.S. Patent No. 5,194,478.

5 However, one disadvantage of sachets is the need for additional packaging operations
6 to add the sachet to each package. A further disadvantage arising from the iron-based
7 sachets is that certain atmospheric conditions (e.g., high humidity, low CO₂ level) in
8 the package are sometimes required in order for scavenging to occur at an adequate
9 rate. Further, the sachets can present a danger to consumers if accidentally ingested.

10 Another means for regulating the exposure to oxygen involves incorporating an
11 oxygen scavenger into the packaging structure itself. A more uniform scavenging
12 effect throughout the package is achieved by incorporating the scavenging material in
13 the package itself instead of adding a separate scavenger structure (e.g., a sachet) to
14 the package. This may be especially important where there is restricted air flow
15 inside the package. In addition, incorporating the oxygen scavenger into the package
16 structure provides a means of intercepting and scavenging oxygen as it permeates the
17 walls of the package (herein referred to as an "active oxygen barrier"), thereby
18 maintaining the lowest possible oxygen level in the package.

19 One attempt to prepare an oxygen-scavenging wall involves the incorporation of
20 inorganic powders and/or salts. See U.S. Patent Nos. 5,153,038, 5,116,660,
21 5,143,769, and 5,089,323. However, incorporation of these powders and/or salts
22 causes degradation of the wall's transparency and mechanical properties such as tear
23 strength. In addition, these compounds can lead to processing difficulties, especially
24 when fabricating thin films. The oxidation products, which can be absorbed by food
25 in the container, typically would not have FDA approval for human consumption.

1 EP 0 519 616 discloses an oxygen-scavenging composition comprising a blend of a
2 first polymeric component comprising a polyolefin, the first polymeric component
3 having been grafted with an unsaturated carboxylic anhydride or an unsaturated
4 carboxylic acid, or combinations thereof, or with an epoxide; a second polymeric
5 component having OH, SH, or NHR² groups where R² is H, C₁-C₃ alkyl, substituted
6 C₁-C₃ alkyl; and a metal salt capable of catalyzing the reaction between oxygen and
7 the second polymeric component, the polyolefin being present in an amount sufficient
8 so that the blend is non phase-separated. A blend of polymers is utilized to obtain
9 oxygen scavenging, and the second polymeric component is preferably a polyamide or
10 a copolyamide such as the copolymer of m-xylylene-diamine and adipic acid (MXD6).

11 The oxygen scavenging systems disclosed in U.S. Patent Nos. 5,021,515, 5,194,478,
12 and 5,159,005, European Publication EP 0 380 319 as well as PCT Publication Nos.
13 90/00504 and 90/00578 illustrate attempts to produce an oxygen-scavenging wall.
14 These patent applications disclose incorporating a metal catalyst-polyamide oxygen
15 scavenging system into the package wall. Through the catalyzed oxidation of the
16 polyamide, the package wall regulates the amount of oxygen which reaches the
17 interior volume of the package (active oxygen barrier) and has been reported to have
18 oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc) oxygen per
19 square meter per day at ambient conditions. However, this system suffers from
20 significant disadvantages.

21 One particularly limiting disadvantage of polyamide/catalyst materials can be a low
22 oxygen scavenging rate. U.S. Patent No. 5,021,515, Example 7, illustrates that
23 adding these materials to a high-barrier package containing air produces a package
24 which is not generally suitable for creating an internal oxygen level of less than 0.1%
25 (starting with air) within a period of four weeks or less at room temperature, as is
26 typically required for headspace oxygen scavenging applications.

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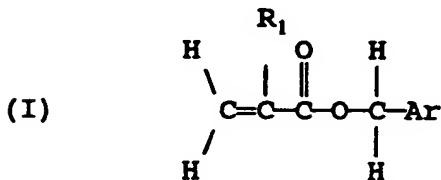
1 There are also disadvantages to having the oxygen-scavenging groups in the backbone
2 or network structure in this type of polyamide polymer. The basic polymer structure
3 degrades rapidly and is quickly weakened upon reaction with oxygen. This can
4 adversely affect physical properties such as tensile or impact strength of the polymer.
5 The degradation of the backbone or network of the polymer can increase the
6 permeability of the polymer to those materials sought to be excluded, such as oxygen.

7 Moreover, polyamides such as MXD6 are typically incompatible with thermoplastic
8 polymers used in flexible packaging walls, such as ethylene-vinyl acetate copolymers
9 and low density polyethylene. Even further, when polyamides are used by themselves
10 to make a flexible package wall, they may result in inappropriately stiff structures.
11 Polyamides also incur processing difficulties and higher costs when compared with the
12 costs of thermoplastic polymers typically used to make flexible packaging. Even
13 further, they are sometimes difficult to heat seal. Thus, all of these are factors to
14 consider when selecting materials for packages, especially flexible packages and when
15 selecting systems for reducing oxygen exposure of packaged products.

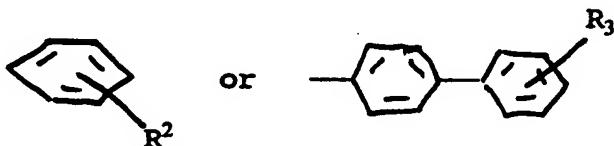
16 Another approach to scavenging oxygen is disclosed in EP 0 507 207, which discloses
17 an oxygen-scavenging composition comprising an ethylenically unsaturated
18 hydrocarbon and a transition metal catalyst. This patent states that ethylenically
19 unsaturated compounds such as squalene, dehydrated castor oil, and 1,2-polybutadiene
20 are useful oxygen scavenging compositions, and ethylenically saturated compounds
21 such as polyethylene and ethylene copolymers are used as diluents. Compositions
22 utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically have an
23 oily texture, which is undesirable for applications such as wrapping meat for sale in
24 retail grocery stores. Further, polymer chains which are ethylenically unsaturated
25 would be expected to either cross-link to become brittle or to degrade upon
26 scavenging oxygen, weakening the polymer in either case.

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1 U.S. Patent Nos. 4,717,759, 4,994,539, and 4,736,007, which are incorporated by
 2 reference in their entirety, disclose ethylene copolymers which comprise 85.0 to
 3 99.995 mol % of an ethylene unit, 0.005 to 5 mol % of a comonomer unit
 4 represented by Formula (I)



11 wherein Ar is



15 R₁ is a hydrogen atom or a methyl group, each of R₂ and R₃ is a hydrogen atom, a
 16 chlorine atom or a straight-chain or a side-chain alkyl group having 1 to 4 carbon
 17 atoms, and 0 to 10 mol % of an ethylenic unsaturated monomer unit, the ethylene
 18 copolymer having a density of 0.860 to 0.970 g/cm³ and a melt index of 0.05 to 100
 19 g/10 minutes. The patent states that copolymers may be produced using either a
 20 Ziegler catalyst or through polymerization catalyzed by free radicals. These polymers
 21 are limited to having less than 5 mol % of the comonomer unit and are useful for
 22 electrical insulation.

23 Transesterification of polymers has also been discussed in the literature. For
 24 example, M. Lambla et al., 27 *Polymer Sci. and Eng'g*, No. 16 (mid-Sept. 1987)
 25 1221-28, discuss the transesterification of ethylene vinyl acetate copolymer with an
 26 alcohol in a reactive extruder and in the presence of a tin catalyst to form ethylene
 27 vinyl alcohol copolymer, which has a polyethylenic backbone and pendant alcohol
 28 moieties.

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1 D. Seebach et al., *Synthesis* (Feb. 1982) 138-41, discuss transesterification of an ester
2 with an alcohol in solution using a titanium catalyst. The reactions require from 3 to
3 120 hours.

4 U.S. Pat. No. 4,767,820 to M. Keogh discloses compositions useful as extrudates
5 about wires and cables which comprise hydrolyzable pendant silane moieties and
6 tetramethyl titanate dispersed in a normally solid alkylene-alkyl acrylate copolymer
7 matrix. Transalkylation of the silane and alkyl acrylate moieties results in a cross-
8 linked product.

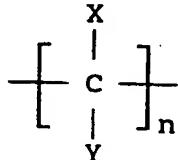
9 U.S. Pat. No. 5,023,284 to M. Cheung et al. notes that transesterification occurs
10 during melt-blending of two polyesters due to the presence of residual titanium
11 catalyst and causes embrittlement and other deleterious effects.

12 What has been missing in the prior art is effective oxygen scavenging compositions
13 that have high scavenging rates and that are compatible with a wide range of
14 polymers. Also missing from the prior art is an economical process for controlling
15 the transesterification of a polymer having a polyethylenic backbone and pendant ester
16 moieties to produce a polymer having a polyethylenic backbone and pendant ester
17 moieties that differ in number and/or type from the unreacted polymer. This
18 invention provides those compositions and that process.

19 **SUMMARY OF THE INVENTION**

20 In one embodiment, the invention provides a composition comprising a transition-
21 metal salt and a component having the structure of Formula (II)

22 (II)



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1 where n is an integer from 2 to approximately 30,000; any X is individually chosen
2 from the group consisting of hydrogen and methyl radical; and where any Y is
3 individually chosen from the group consisting of hydrogen, alkyl radicals containing
4 from 1 to 18 carbon atoms, alkoxy radicals having from 1 to 16 carbon atoms, amine
5 radicals having from 1 to 6 carbon atoms, ester and amide radicals of acids having
6 from 1 to 16 carbon atoms, aryl radicals or substituted aryl radicals having 6 to 24
7 carbon atoms, aryl ether radicals or substituted aryl ether radicals having from 6 to 24
8 carbon atoms, and the radicals of Formula III and Formula IV

9
10 (III)
11
12 | A
| B

where any A is individually a heteroatom-containing radical, and where any B is individually chosen from the group consisting of the radicals of Formula V and Formula VI:

20
 21
 22 (V)

23

24		
25	(VI)	
26		

1 where any R¹, R², R³, R⁴, R⁵, and R⁶ is individually chosen from the group
2 consisting of hydrogen, alkyl radicals containing from 1 to 18 carbon atoms, alkoxy
3 radicals having from 1 to 16 carbon atoms, amine radicals having from 1 to 6 carbon
4 atoms, ester and amide radicals of acids having from 1 to 16 carbon atoms, aryl
5 radicals or substituted aryl radicals having 6 to 24 carbon atoms, aryl ether radicals or
6 substituted aryl ether radicals having from 6 to 24 carbon atoms, and the radicals of
7 Formula III and Formula IV; with the proviso that when Y is an acetate radical, X is
8 hydrogen; and with the further proviso that at least 1 mole % of the composition
9 comprises the radicals of Formula III and Formula IV.

10 In another embodiment, the invention provides a composition comprising a transition-
11 metal salt and an ethylenic backbone having a pendant or terminal benzyl radical,
12 wherein the composition produces benzoic acid or a benzoic acid substituted with at
13 least one radical selected from the group consisting of alkyl radicals containing from 1
14 to 18 carbon atoms, alkoxy radicals having from 1 to 16 carbon atoms, amine radicals
15 having from 1 to 6 carbon atoms, ester and amide radicals of acids having from 1 to
16 carbon atoms, aryl radicals or substituted aryl radicals having 6 to 24 carbon
17 atoms, and aryl ether radicals or substituted aryl ether radicals having from 6 to 24
18 carbon atoms upon reaction with molecular oxygen.

19 In another embodiment, the invention provides a composition comprising a transition-
20 metal salt and a polymer, where said polymer comprises 1) a polyethylenic backbone,
21 and 2) pendant moieties which have at least one radical selected from the group
22 consisting of a) benzyl ester radicals, b) N-benzyl-amide radicals, c) N-benzylimide
23 radicals, d) benzyl-thio radicals, e) benzyl ketone radicals, f) benzyl-ether radicals,
24 g) aryl radicals or substituted aryl radicals having 6 to 30 carbon atoms, h) aryl ether
25 radicals or substituted aryl ether radicals having from 6 to 30 carbon atoms, and
26 i) benzyl radicals which have the phenyl radical of said benzyl radical chemically
27 bonded to at least one member selected from the group consisting of imide radicals

1 which are N-substituted with said benzyl radicals, benzyl-ketone radicals, alkyl
2 radicals containing from 1 to 18 carbon atoms, alkoxy radicals having from 1 to 16
3 carbon atoms, amine radicals having from 1 to 6 carbon atoms, ester and amide
4 radicals of acids, said ester and amide radicals having from 1 to 16 carbon atoms,
5 aryl radicals or substituted aryl radicals having 6 to 24 carbon atoms, and aryl ether
6 radicals or substituted aryl ether radicals having from 6 to 24 carbon atoms.

7 In one embodiment, the invention provides new compositions comprising a transition-
8 metal salt and a polymer which comprises a polyethylenic backbone and a pendant
9 moiety comprising a benzyl radical. In another embodiment, the invention provides
10 new polymeric compositions useful in making oxygen scavenging compositions.
11 Methods of making and using the compositions of the present invention are also
12 disclosed.

13 Among other factors, the present invention is based on our finding that compositions
14 as described herein are highly effective oxygen scavengers in terms of rate of oxygen
15 scavenging and/or oxygen scavenging capacity, particularly where the compositions
16 contain a heteroatom-containing radical directly bonded to a benzyl radical.
17 Furthermore, in many instances, these compositions have excellent physical and
18 processing properties which permit their incorporation into a wide range of packaging
19 applications. Also, we have found that, typically, films of these compositions are
20 easily made using conventional techniques. Still further, the compositions also are
21 usually compatible with many common thermoplastic materials used in packaging,
22 particularly polyethylene and copolymers of ethylene and alkyl acrylates or
23 methacrylates.

24 Furthermore, many of the compositions of the present invention have been found to
25 have surprisingly reduced induction periods in scavenging oxygen upon exposure to
26 ultraviolet (UV) radiation without the need for added photo-initiators.

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1 Also, this invention comprises the process of forming a melt of a polymer having a
2 polyethylenic backbone and pendant ester moieties, and contacting the melt with a
3 transesterifying compound in a reactive extruder under transesterification conditions,
4 where the polymer undergoes transesterification but not alcoholysis, and the polymer
5 after transesterification has an polyethylenic backbone and pendant ester moieties.
6 The process may further comprise adding an amount of transition metal salt in an
7 amount effective to promote oxygen scavenging by the transesterified polymer. The
8 process may also further comprise exposing the transesterified polymer to actinic
9 radiation, thereby reducing the induction period of the composition to scavenging
10 oxygen.

11 In one preferred embodiment, an ethylene alkyl acrylate copolymer is transesterified
12 in a reactive extruder to form an ethylene hydrocarbyl acrylate copolymer. In another
13 preferred embodiment, a cobalt salt is added to the transesterified polymer to make an
14 effective oxygen scavenger. In a third preferred embodiment, the processed polymer
15 is exposed to actinic radiation.

16 Among other factors, it has been discovered that a reactive extruder can effectively
17 transesterify a polymer having pendant ester moieties and a transesterifying compound
18 to produce a polymer having pendant ester moieties which differ in number and/or
19 type from the unreacted polymer. This transesterification process provides accurate
20 control over the extent of transesterification and fast reaction times, thereby providing
21 an economical means to produce polymers having properties tailored to specific
22 applications. The process also provides a means to make highly-effective oxygen
23 scavenging compositions.

24 The above-mentioned advantages and others are further described below.

1 DESCRIPTION OF THE DRAWINGS

2 Figure 1 illustrates the effect on oxygen scavenging rate when substituting methyl or
3 methoxy radicals onto the phenyl ring.

4 Figure 2 illustrates the oxygen scavenging capacity for polymer of Example 19.

5 Figure 3 compares the scavenging rate and capacity of polymer of Example 19 with
6 Ageless, a product available from Mitsubishi Gas Chemical Co.

7 Figure 4 illustrates the effect of various cobalt levels on the oxygen scavenging rate.

8 Figure 5 compares the oxygen transmission rate for two 3-layer films, one utilizing
9 polymer from Example 25 and one using polymer from Example 19. These rates are
10 compared to the theoretical oxygen transmission rate of a 2-mil thick film of ethylene-
11 vinyl alcohol copolymer resin.

12 DETAILED DESCRIPTION

13 In one embodiment, the compositions of the present invention are effective to
14 scavenge oxygen. The term "scavenge" means to absorb, deplete, or react with
15 oxygen so that a substantial amount of oxygen does not return to the environment
16 from which it was absorbed, depleted, or reacted. A material which absorbs at least
17 0.5 cc of oxygen per gram of composition per day is considered to be oxygen-
18 scavenging.

19 Also, many of the compositions of the present invention have good adhesive
20 properties. These compositions can bind layers of materials together or can be used
21 as a coating on articles to provide a surface capable of binding. These compositions
22 can also be effective as a heat-seal layer.

1 DESCRIPTION OF THE COMPOSITIONS OF THE PRESENT INVENTION

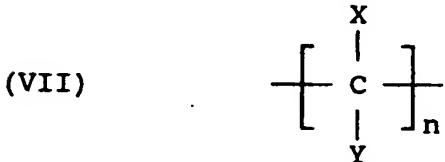
2 In one embodiment, the compositions of the present invention comprise a transition-
3 metal salt and a component having an ethylenic backbone and having pendant or
4 terminal moieties which contain a benzyl radical.

5 A transition-metal salt, as the term is used herein, comprises an element chosen from
6 the first, second and third transition series of the periodic table of the elements. This
7 transition-metal salt is in a form which facilitates or imparts scavenging of oxygen by
8 the composition of this invention. It is generally believed that the transition-metal salt
9 is in an ionic state such that the transition element can readily inter-convert between
10 at least two oxidation states. Suitable transition-metal elements include, but are not
11 limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III, copper I
12 or II, rhodium II, III or IV, and ruthenium. The oxidation state of the transition-
13 metal element when introduced into the composition is not necessarily that of the
14 active form. It is only necessary to have the transition-metal element in its active
15 form at or shortly before the time that the composition is required to scavenge
16 oxygen. The transition-metal element is preferably iron, nickel or copper, more
17 preferably manganese and most preferably cobalt.

18 Suitable counter-ions for the transition metal element are organic or inorganic anions.
19 These include, but are not limited to, chloride, acetate, stearate, palmitate,
20 2-ethylhexanoate, citrate, glycolate, benzoate, neodecanoate or naphthenate. Organic
21 anions are preferred. Particularly preferable salts include cobalt (II)
22 2-ethylhexanoate, cobalt benzoate, and cobalt (II) neodecanoate. The transition-metal
23 element may also be introduced as an ionomer, in which case a polymeric counter-ion
24 is employed. Such ionomers are well known in the art. See U.S. Patent
25 No. 3,264,272, which is incorporated by reference in its entirety.

1 The composition of the present invention contains a sufficient quantity of the
2 transition-metal salt to promote oxygen scavenging in the polymer. Generally, this
3 requires a ratio of moles of benzyl radicals to moles of transition-metal element -
4 between about 2000:1 to about 10:1. Preferably, this molar ratio is between 200:1
5 and 20:1. The preferred amount of transition-metal element will typically vary with
6 which transition-metal salt is used.

The composition of the present invention also comprises a component which comprises an ethylenic backbone. In one embodiment, the composition may be of low molecular-weight and have a benzyl group pendant or terminal to the ethylenic backbone. The backbone may have one ethylene unit or may be an oligomer or very low molecular weight polymer having a melt index greater than about 1000 grams per 10 minutes. Examples include benzyl, dibenzyl or tribenzyl esters of C₁-C₂₀ acids, such as citric acid, ascorbic acid, stearic acid and 1,10-decanedicarboxylic acid. In another embodiment, the composition has a polyethylenic backbone having a melt index within the range of about 0.3 to about 1000 grams per 10 minutes (ASTM Method No. D-882). Preferably, the melt index is between about 0.5 and about 100, and more preferably is between about 1 and about 10 g/10 min. A polyethylenic backbone consists essentially of a chain structure or backbone of saturated carbon atoms which, generally, is created during a polymerization process. For example, homopolymerization of ethylene provides a polyethylenic backbone.



29 provides a polymer having a polyethylenic backbone.

1 The composition of the present invention also comprises moieties which contain a
2 benzyl radical and which are pendant or terminal to the ethylenic backbone. A
3 pendant moiety which contains a benzyl radical, as that term is used herein, is any
4 group which is a side-chain or branch or is terminal to the ethylenic backbone and
5 which contains a benzyl radical. In Formula (VII) above, moieties -X and -Y are
6 pendant moieties.

7 The benzyl radical comprises a phenyl radical directly bonded to a methylene radical.
8 These radicals may be substituted with a hydrocarbyl radical or a heteroatom or
9 heteroatom-containing radical or may be unsubstituted. A substituted phenyl radical
10 has at least one radical substituted in place of at least one hydrogen atom of the
11 phenyl radical. An unsubstituted methylene radical, for the purposes of this
12 invention, consists of one carbon atom and two or three hydrogen atoms. A
13 substituted methylene radical, for the purposes of this invention, consists of one
14 carbon atom, one hydrogen atom, and at least one radical substituted in place of one
15 of the hydrogen atoms. A benzyl radical may be bonded to the remainder of its
16 pendant moiety through its phenyl radical. In this case, its methylene radical may be
17 a methyl radical or a substituted methyl radical.

18 A heteroatom-containing radical is any radical which contains an element other than
19 carbon and hydrogen. The heteroatom-containing radical generally improves the
20 oxygen-scavenging abilities of the composition. When present, the heteroatom-
21 containing radical is preferably bonded directly to the benzyl radical with no moieties
22 present between the heteroatom-containing radical and the benzyl radical. The
23 heteroatom-containing radical may be bonded to the benzyl radical in any combination
24 of three possible ways. For example, the heteroatom-containing radical may be
25 bonded to the methylene radical. It may also be substituted onto the methylene
26 radical in place of one of the hydrogen atoms, in which case the methylene radical is
27 attached directly to the backbone or the moiety attached to the backbone or to another

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1 heteroatom-containing moiety. Or, the heteroatom-containing radical may be
2 substituted in place of one of the hydrogen atoms of the phenyl radical. Examples of
3 heteroatom-containing radicals include amine, ether, sulfide, and ketone radicals, and
4 preferred radicals are esters and amides.

5 Radicals which may be substituted onto the benzyl radical include alkyl radicals
6 containing from 1 to 18 carbon atoms, alkoxy radicals having from 1 to 16 carbon
7 atoms, amine radicals having from 1 to 6 carbon atoms, aryl radicals or substituted
8 aryl radicals having 6 to 24 carbon atoms, aryl ether radicals or substituted aryl ether
9 radicals having from 6 to 24 carbon atoms, and ester and amide radicals of acids
10 having from 1 to 16 carbon atoms. Aryl and aryl ether radicals can be substituted in
11 the same manner as the methylene and the phenyl radicals, subject to the limitation
12 that the aryl and aryl ether radicals, after substitution, have 6 to 24 carbon atoms
13 total. Preferably, the radicals which are substituted onto the benzyl radical are
14 selected from the group consisting of alkyl radicals containing from 1 to 6 carbon
15 atoms, alkoxy radicals having from 1 to 6 carbon atoms, amine radicals having from
16 1 to 6 carbon atoms, aryl radicals or substituted aryl radicals having 6 to 15 carbon
17 atoms, aryl ether radicals or substituted aryl ether radicals having from 6 to 15 carbon
18 atoms, and ester and amide radicals of acids having from 1 to 6 carbon atoms.
19 Preferred radicals which provide higher oxygen scavenging rates are alkyl, alkoxy,
20 and amine radicals.

21 Preferably, the moieties which are pendant to the ethylenic backbone comprise benzyl
22 thioester, more preferably benzyl amide, and most preferably benzyl ester moieties.
23 Preferably, the amide or ester is bonded directly to the ethylenic backbone. Other
24 preferable pendant moieties contain benzyl ether groups, benzyl amine groups, and -
25 CH₂-aryl containing groups where the aryl group includes more than one ring, such
26 as 1,3-dihydroisoindole, anthracene, phenanthrene, naphthalene and the like.

1 Without limiting the invention to this theory, it is believed that the transition metal
2 element catalyzes a reaction between the benzyl radicals in the pendant moieties and
3 oxygen. In one preferred embodiment, this reaction results in scission of the bond
4 between the methylene radical of the benzyl radical and the heteroatom-containing
5 radical. This reaction forms a separate compound, a benzoic acid, a salt of a benzoic
6 acid, or a substituted benzoic acid or salt. Preferably, benzoic acid is formed, which
7 is listed by the FDA as a compound generally regarded to be safe for human
8 consumption in limited quantities.

9 It is believed that the primary function of the benzyl radicals is to react irreversibly
10 with oxygen during the scavenging process. The primary function of the transition-
11 metal salt is to facilitate this process. Thus, to a large extent, the quantity of benzyl
12 radicals and the amount of transition-metal salt will affect the rate at which oxygen is
13 consumed. Thus, the quantities of benzyl radicals and transition-metal salt are
14 selected in accordance with the scavenging rate needed.

15 In one preferred embodiment, a polymeric composition of the present invention
16 contains between about one and ten mole percent benzyl radicals. More preferably,
17 the composition contains between about two and six percent, and more preferably
18 still, between about two and three mole percent benzyl radicals. Preferably, the
19 benzyl radicals are bonded directly to a heteroatom-containing group. The exact
20 amount of benzyl radicals and heteroatom-containing radicals as well as the amount of
21 transition-metal salt are normally determined by the application in which the
22 composition is going to be employed.

23 In another preferred embodiment, a composition of the present invention comprises a
24 terpolymer of ethylene, a benzylic acrylate or acrylamide, and an alkyl acrylate, alkyl
25 methacrylate, acrylic acid, or methacrylic acid. This type of composition has a
26 polyethylenic backbone which is substituted with alkyl ester or acid moieties as well

1 as scavenging moieties. Scavenging moieties, for the purpose of this invention,
2 consist of the benzyl radicals and substituted benzyl radicals and additionally any
3 heteroatom-containing radicals bonded to the benzyl radicals or substituted radicals, as
4 defined previously. Preferred alkyl acrylates are butyl and ethyl acrylate, and most
5 preferred is methyl acrylate (MA). Preferred acrylic acids are acrylic acid and
6 methacrylic acid. These ester and acid moieties can provide good adhesive properties
7 in tie layers, for example.

8 The polymeric compositions of the present invention may also be ionomers which
9 contain salts of an alkyl ester or acid. Sodium, potassium, zinc, and lithium salts are
10 preferred.

11 Additives may also be included in the composition to impart properties desired for a
12 particular use. Such additives include, but are not necessarily limited to, fillers,
13 pigments, dyestuffs, antioxidants, stabilizers, processing aids, plasticizers, fire
14 retardants, anti-fog agents, etc. The amount of these additives vary by use and
15 typically comprise less than 10%, and preferably less than 5%, of the total weight of
16 the composition.

17 One additive that may be included in the composition is a photoinitiator, which acts to
18 reduce the induction period of many oxygen scavenging compositions. See U.S.
19 Patent No. 5,211,875, which discusses photoinitiators and which is incorporated by
20 reference in its entirety.

21 **METHODS OF MAKING THE COMPOSITIONS OF THE PRESENT INVENTION**
22 Compositions of the present invention having an ethylenic backbone and pendant
23 moieties comprising benzyl radicals can be made by many means. Typically, the
24 process comprises incorporating a transition-metal salt into the ethylenic scavenging
25 component.

1 There are many ways to make the ethylenic component of the compositions of the
2 present invention. Monomers containing benzyl radicals can be homopolymerized or
3 copolymerized with ethylene, propylene or other olefins to provide an ethylenic
4 backbone after polymerization. Methods for this type of polymerization are well-
5 known in the art and include solution, slurry, or gas-phase polymerization in the
6 presence of a catalyst, such as a free radical catalyst, a Ziegler Natta catalyst, or a
7 metallocene polymerization catalyst.

8 A preferred way to make a polymer component is to produce a polymer intermediate
9 and react the intermediate with a suitable benzylic compound to form the polymer
10 component. The transition-metal salt can be incorporated into the composition before,
11 during, or after reacting the polymer intermediate with the benzylic compound.

12 There are many types of polymer intermediates which are useful in making
13 compositions of the present invention. For example, an alkyl methacrylate can be
14 homopolymerized by way of addition polymerization to form a polymer having an
15 ethylenic backbone with pendant methyl groups and with pendant alkyl ester groups.
16 Copolymerization of ethylene with an alkyl acrylate or methacrylate also forms a
17 useful polymer intermediate. One preferred copolymer is ethylene methyl acrylate
18 copolymer, sold by Chevron Chemical Company as EMAC® copolymer.

19 High melt-point ethylene-alkyl acrylate copolymers are also useful polymer
20 intermediates. These copolymers have a melt-point temperature at least about 6 deg F
21 greater than a reference ethylene-alkyl acrylate copolymer, where the reference
22 copolymer is made in a multi-zone autoclave reactor and the ratio of alkyl acrylate to
23 ethylene in a reaction zone when making the reference copolymer is about equal to
24 the overall ethylene to alkyl acrylate ratio fed to the multi-zone autoclave reactor. A
25 high melt-point ethylene-methyl acrylate copolymer typically has a melt-point
26 temperature greater than the value obtained from the expression:

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1 temperature (deg F) = 248 - 2.9Y

2 where Y is the weight percent of methyl acrylate in the high melt-point ethylene-
3 methyl acrylate copolymer and where Y is greater than 10. Similarly, a high melt-
4 point ethylene-butyl acrylate copolymer typically has a melt-point temperature greater
5 than the value obtained from the expression:

6 temperature (deg F) = 240 - 2.1Z

7 where Z is the weight percent of butyl acrylate in the high melt-point ethylene-butyl
8 acrylate copolymer and where Z is greater than 15. High melt-point ethylene-alkyl
9 acrylate copolymers can be made by a process comprising:

- 10 A. feeding overall an amount by weight, A, of alkyl acrylate and an
11 amount by weight, E, of ethylene to a multi-zone autoclave
12 polymerization reactor;
- 13 B. introducing an effective amount of an initiator and at least a portion,
14 E₁, of the total amount of ethylene into a first reaction zone of the
15 reactor;
- 16 C. concurrently introducing a portion, A₁, of alkyl acrylate to said first
17 reaction zone such that the ratio A₁/E₁ is at least about 20% more than
18 or is at least about 20% less than the ratio A/E for the reactor overall;
19 and
- 20 D. feeding any remaining portions of initiator, ethylene and alkyl acrylate
21 to a subsequent reaction zone or zones.

22 High melt-point ethylene-alkyl acrylate copolymers are disclosed in U.S. Ser. Nos.
23 07/764,861, filed Sep. 24, 1991, 07/947,870, filed Sep. 21, 1992, and 08/233,180,
24 filed Apr. 26, 1994, which are incorporated by reference herein in their entirety.

1 Another useful polymer intermediate is ethylene vinyl acetate copolymer. Yet another
2 polymer intermediate is a polyethylenic-backbone polymer containing maleic
3 anhydride moieties. For example, Lotader, a product of ELF Atochem, contains
4 ethylene, alkyl acrylate and maleic anhydride moieties in which the unsaturated
5 carbon atoms of maleic anhydride become saturated carbon atoms within the
6 polyethylenic backbone. Alternatively, maleic anhydride may be grafted to a polymer
7 having a polyethylenic backbone by, for example, free-radical grafting. Methods for
8 making these polymers are well-known in the art. See, for example, U.S. Patent
9 No. 4,506,056, which is incorporated by reference in its entirety. An ester, acid,
10 acetate, or anhydride in the moieties pendant to the polyethylene backbone is then
11 reacted with a benzylic compound to form a polymer useful in the compositions of the
12 present invention.

13 The benzylic compound which is reacted with the polymer intermediate is selected on
14 the basis of its reactivity with the particular polymer intermediate and on the basis of
15 whether a heteroatom-containing radical is desired to improve the reactivity of the
16 benzyl radical with oxygen. The benzylic compound may be substituted or
17 unsubstituted, as discussed previously. In a preferred embodiment of this invention, a
18 polymer intermediate having pendant methyl acrylate moieties, ethylene-methyl
19 acrylate copolymer, is transesterified with benzyl alcohol to form pendant benzyl
20 acrylate moieties. Likewise, in another preferred embodiment, ethylene-methyl
21 acrylate copolymer is transamidated with benzyl amine to form pendant benzyl-amide
22 moieties. Benzyl alcohol is available from Akzo Chemical Company, and benzyl
23 amine is available from Spectrum Chemical Company. In these cases, the important
24 feature of the benzylic compound is that it is capable of transesterification or
25 transamidation under conditions sufficient to promote such transesterification or
26 transamidation.

1 Imidation (the reaction of an anhydride with a primary amine to form an imide),
2 transesterification, or transamidation may be performed in an autoclave. Reaction
3 conditions will vary, depending on the reactants. A transesterification or
4 transamidation catalyst may be used. For a polymer intermediate having alkyl
5 acrylate or methacrylate pendant moieties, typically the reaction will be performed at
6 a temperature between 180 and 300°C and at a pressure of between 50 and 1000 psi
7 for a period of time between ½ and 8 hours. Preferably, the reaction will be
8 performed at a temperature between 200 and 240°C and at a pressure of between 100
9 and 600 psi for a period of time between 1 and 5 hours where ethylene-methyl
10 acrylate copolymer is reacted with benzyl amine. This produces a polymer containing
11 pendant moieties comprising benzyl radicals. Amidation of an acid or transamidation
12 may also be performed in a reactive extruder, as discussed below.

13 Esterification, transesterification, transamidation, or imidation may also be performed
14 by dissolving an ethylenic component such as a polymer in a solvent and heating the
15 component, the benzylic compound (e.g. benzyl amine or benzyl alcohol), and
16 optionally the transesterification or transamidation catalyst at reflux conditions. The
17 conditions can vary, depending on the particular composition sought. Typically the
18 reaction will be performed at a temperature between 130 and 240°C for a period of
19 time between ½ and 16 hours. Preferably, the reaction will be performed at a
20 temperature between 160 and 200°C for a period of time between 1 and 8 hours
21 where ethylene-methyl acrylate copolymer is reacted with benzyl alcohol. This also
22 produces a polymer containing pendant moieties comprising benzyl radicals. This
23 method is useful for esterifying low molecular-weight acids with a benzylic alcohol.

24 Esterification or transesterification can be facilitated by use of transesterification
25 catalysts, which are well-known in the art. Suitable transesterification catalysts
26 include strong non-oxidizing acids, Group I alkoxides, and Group IVB alkoxides,
27 such as di-butyl tin dilaurate, sodium methoxide, toluene sulfonic acid, tetrabutyl

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1 titanate, tetraisopropyl titanate, and tetraethyl titanate, with tetraalkyl titanate being
2 particularly preferred. Titanate catalysts are available from Hüls America.

3 Likewise, transamidation can be facilitated by use of transamidation catalysts, which
4 are well-known in the art. Suitable transamidation catalysts include 2-hydroxy
5 pyridine and sodium methoxide, with 2-hydroxy pyridine being particularly preferred.
6 These catalysts are available from Aldrich.

REACTIVE EXTRUSION

7 A particularly preferred method of making ester or imide compositions of the present
8 invention is through reactive extrusion. In this process, a composition of the present
9 invention or preferably the ethylenic component of a composition of the present
10 invention is made by melt-blending a polymer intermediate with a benzylic-containing
11 compound and, optionally, with the transesterification and/or transamidation catalyst
12 and, also optionally, the transition-metal salt. Reaction conditions are chosen to
13 promote esterification, transesterification and/or imidation. Esterification and
14 transesterification preferably occurs using a transesterification catalyst. The resulting
15 polymer can be extruded into any convenient form, such as pellets or film. The
16 reactive extrusion process is discussed in further detail below.

1. THE POLYMER FED TO THE REACTIVE EXTRUDER

17 The polymer fed to the reactive extruder, also referred to herein as an ethylene
18 copolymer, has a polyethylenic backbone and pendant ester and/or acid moieties.
19 This polymer has a melt index within the range of about 0.3 to about 1000 grams per
20 10 minutes (ASTM Method No. D-882). Preferably, the melt index is between about
21 0.5 and about 100, and more preferably is between about 1 and about 10 g/10 min.

22
23
24 The ethylene copolymer also contains ester and/or acid groups or radicals which are
25 pendant to the polyethylenic backbone. A pendant moiety which contains an ester or

- 1 acid radical is any group which is a side-chain or branch to the polyethylenic
2 backbone and which contains an ester radical, an acid radical, or a radical that can be
3 considered to be equivalent to an acid, such as an anhydride. In Formula (I) above,
4 the moieties X and Y are pendant moieties.
- 5 The hydrocarbyl radical on the ester is one which is capable of being transesterified
6 under transesterification conditions by the transesterifying compound and the optional
7 transesterification catalysts. The ester radical preferably has an unsubstituted
8 hydrocarbyl radical. An unsubstituted hydrocarbyl radical for the purposes of this
9 invention includes a C₁-C₈ alkyl, preferably C₁-C₄ alkyl, and more preferably a
10 methyl radical.
- 11 The ester radical may have a hydrocarbyl radical that is substituted with a heteroatom
12 or a heteroatom-containing radical. A heteroatom is an element other than carbon and
13 hydrogen. Examples of a substituted hydrocarbyl radical on unreacted ethylene
14 copolymers are methoxy ethyl and mono-methoxy polyethylene glycol.
- 15 The ethylene copolymer fed to the reactive extruder contains a major portion of
16 ethylene. Typically, the ethylene copolymer contains from about 83 to about 99.7
17 mole percent ethylene, based on all comonomers present in the polymer. Preferably,
18 the polymer contains about 90.7 to 98 mole percent, and more preferably, contains 93
19 to 97 mole percent ethylene.
- 20 In one preferred embodiment, the polymer fed to the reactive extruder is an ethylene
21 alkyl acrylate copolymer. As used herein, the term "ethylene alkyl acrylate
22 copolymer" also includes ethylene-alkyl methacrylate copolymer and ethylene-alkyl
23 acrylate-alkyl methacrylate copolymer. Ethylene-alkyl acrylate copolymers and
24 methods of making them are well-known in the art. Particularly preferred is

1 ethylene-methyl acrylate copolymer. High melt-point ethylene-alkyl acrylate
2 copolymers are also useful polymer intermediates.

3 In another preferred embodiment, the polymer fed to the reactive extruder is an
4 ethylene vinyl acetate copolymer, an ethylene acrylic acid copolymer or an ethylene
5 copolymer containing pendant groups which are equivalent to acid moieties, such as
6 anhydrides.

7 The ethylene copolymer may optionally contain other comonomers which, when
8 present in the polymer, do not interfere with the transesterification reaction. The
9 optional comonomers may react with the transesterifying compound, but interference
10 for the purposes of this invention occurs when less than 5 % of the ester moieties in
11 the polymer that would have otherwise transesterified if the optional comonomer was
12 not present transesterify in the presence of a stoichiometric excess of transesterifying
13 compound because of the presence of the optional comonomer.

14 One example of an ethylene copolymer having other comonomers which do not
15 interfere with the transesterification reaction is a partially saponified ethylene alkyl
16 acrylate copolymer. Sodium, lithium, or potassium ionomers of an ethylene alkyl
17 acrylate copolymer are described in U.S. Ser. No. 08/144,173, filed Oct. 27, 1993,
18 which is incorporated by reference in its entirety. Preferred is ethylene-methyl
19 acrylate-sodium acrylate copolymer having between about 1 and about 17 mole
20 percent methyl acrylate and about 1 and about 9 mole percent sodium acrylate.
21 Another example is Lotader, a product of ELF Atochem, which is an ethylene alkyl
22 acrylate copolymer which contains maleic anhydride moieties whose unsaturated
23 carbon atoms became saturated carbon atoms within the polyethylenic backbone.
24 Alternatively, maleic anhydride may be grafted to a polymer having a polyethylenic
25 backbone by, for example, free-radical grafting. Methods for making these polymers

1 are well-known in the art. See, for example, U.S. Patent No. 4,506,056, which is
2 incorporated by reference in its entirety.

3 **2. THE TRANSESTERIFYING COMPOUND**

4 The term "transesterifying compound" includes compounds which transesterify with a
5 second compound as well as compounds which esterify a second compound. The
6 transesterifying compound is selected from compounds having the ability to participate
7 in an esterification or transesterification reaction for the particular ethylene copolymer
8 chosen for the reaction. The transesterifying compound may itself be a polymer that
9 is capable of supplying a hydrocarbyl radical to the ethylene copolymer chosen for
10 transesterification. In this way, hydrocarbyl groups may be interchanged between the
11 two polymers, or the two polymers may become cross-linked with one another.

12 The hydrocarbon radical of the transesterifying compound includes alkyl radicals
13 containing from 1 to 18 carbon atoms, aryl radicals or substituted aryl radicals having
14 6 to 24 carbon atoms, and aryl ether radicals or substituted aryl ether radicals having
15 from 6 to 24 carbon atoms.

16 For example, when the ethylene copolymer is an ethylene alkyl acrylate copolymer or
17 an ethylene acrylic acid copolymer, the transesterifying compound may be an alcohol,
18 a diol, a polyol, and ether-ol, an ene-ol, a polyethylene glycol, a hydroxyl-terminated
19 polycarbonate or hydroxyl-containing asphalt. Alcohols are preferred transesterifying
20 compounds for these copolymers. Benzyl alcohol is particularly preferred when
21 making adhesives and oxygen scavenging compounds.

22 When the ethylene copolymer is an ethylene vinyl acetate copolymer, the
23 transesterifying compound may be an organic acid, such as C₁-C₁₆ acid, C₁-C₁₂ diacid
24 and triacid, for example, oleic acid, stearic acid, benzoic acid and citric acid. Phenyl
25 acetic acid is particularly preferred. However, the transesterifying compound for an

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1 ethylene vinyl acetate copolymer is not an alcohol or other compound which removes
2 the carboxy radical from the ethylene copolymer, resulting in an ethylene vinyl
3 alcohol copolymer. It is an essential feature of this invention that the polymer have a
4 polyethylenic backbone and pendant ester moieties after transesterification.

5 The amount of transesterifying compound is typically between about 0.05 mole of
6 hydrocarbyl radical from the transesterifying compound per mole of ester on the
7 ethylene copolymer to 2 moles per mole. Preferably, the amount of transesterifying
8 compound is at or slightly in excess of the stoichiometric amount required to obtain
9 the desired extent of transesterification of ester moieties. The transesterifying
10 compounds are usually liquids for which no solvent is required, although some
11 transesterifying compounds such as hexadecanol are solid. A solid compound may be
12 fed to the extruder neat, or it may be fed to the extruder in a suitable solvent, so long
13 as the compound is mixed uniformly in the melt. The amount of liquid fed to the
14 extruder is preferably minimized so that downstream processing to remove the liquid
15 is not required.

16 The hydrocarbyl radical of the transesterifying compound may be a hydrocarbyl
17 radical or may be a hydrocarbyl radical substituted with a heteroatom or a
18 heteroatom-containing radical. A heteroatom is any element other than carbon and
19 hydrogen.

20 When the process is used to make an oxygen-scavenging composition, an electron-
21 donating group such as a heteroatom or heteroatom-containing radical generally
22 improves the oxygen-scavenging abilities of the composition. When present, the
23 heteroatom or heteroatom-containing radical is preferably bonded directly to the
24 hydrocarbyl radical of the transesterifying compound with no moieties present
25 between the heteroatom or heteroatom-containing radical and the pendant radical.
26 One oxygen scavenging composition which is preferred is an ethylene-benzyl ester

1 copolymer. In this case, the heteroatom-containing radical may be bonded to the
2 benzyl radical in any of three possible ways. The heteroatom-containing radical may
3 be bonded to the methylene radical of the benzyl moiety. It may also be substituted
4 onto the methylene radical in place of one of the hydrogen atoms, in which case the
5 methylene radical is attached directly to the backbone or the moiety attached to the
6 backbone or to another heteroatom-containing moiety. Or, the heteroatom-containing
7 radical may be substituted in place of one of the hydrogen atoms of the phenyl
8 radical. Examples of heteroatom-containing radicals include amine, ether, sulfide,
9 and ketone radicals, and preferred radicals are esters and amides. Aryl and aryl ether
10 radicals can be substituted in the same manner on the methylene and the phenyl
11 radicals, subject to the limitation that the aryl and aryl ether radicals, after
12 substitution, have 6 to 24 carbon atoms total. Preferably, the radicals which are
13 substituted onto the benzyl radical are selected from the group consisting of alkyl
14 radicals containing from 1 to 6 carbon atoms, alkoxy radicals having from 1 to 6
15 carbon atoms, amine radicals having from 1 to 6 carbon atoms, aryl radicals or
16 substituted aryl radicals having 6 to 15 carbon atoms, aryl ether radicals or substituted
17 aryl ether radicals having from 6 to 15 carbon atoms, and ester and amide radicals of
18 acids having from 1 to 6 carbon atoms. Preferred radicals which provide higher
19 oxygen scavenging rates are alkyl, alkoxy, and amine radicals that are bonded to the
20 methylene radical of the benzyl moiety, or that are bonded in the ortho and/or para
21 position on the phenyl moiety.

22 3. TRANSESTERIFICATION PROCESS

23 The ethylene copolymer is transesterified in a reactive extruder. In this process, a
24 melt of a polymer having a polyethylenic backbone and pendant ester moieties is
25 mixed with a transesterifying compound and, optionally, a transesterification catalyst
26 and/or an oxygen scavenging-promoting transition-metal salt in a reactive extruder.
27 Reaction conditions are chosen to promote transesterification. Transesterification
28 preferably occurs using a transesterification catalyst. The resulting polymer can be

- 1 extruded into any convenient form, such as pellets or film, and may be exposed to
2 actinic radiation.
- 3 A melt-blend is preferably made by introducing solid ethylene copolymer (such as
4 ethylene-methyl acrylate copolymer pellets) into a reactive extruder at a temperature
5 and mixing time sufficient to melt the polymer and blend it with the transesterifying
6 compound and any catalysts and transition-metal salts which are optionally introduced
7 into the reactive extruder. A melt may also be formed outside the reactive extruder
8 and fed into the reactive extruder. The appropriate temperature for melt-blending is
9 within the temperature range established by the melting temperature of the polymer
10 and the temperature at which the polymer starts to degrade. Typically, the
11 temperature is between 180 and 250°C. The blend time, which is the length of time
12 required to mix or blend the polymer, transesterifying compound, and optional
13 catalyst and transition-metal salt, is chosen to provide good mixing and significant
14 reaction of the transesterifying compound with the polymer. Typically, the blend
15 time is between 5 seconds and 2 minutes in the reactive extruder.
- 16 Little or no solvent is used beyond that amount needed to assure good contact of the
17 transesterifying compound with the melt. Alcohols and organic acids typically are
18 liquids at reaction conditions, so no solvent is necessary for these transesterifying
19 compounds. The transesterification reaction can proceed without using a polymer
20 solvent, since the polymer melt and intensive mixing supplied by the extruder provide
21 sufficient contact between the polymer and the transesterifying compound.
- 22 The degree of reaction of the ethylene copolymer is preferably based on the amount
23 of transesterifying compound added. Preferably, the transesterifying compound
24 completely reacts with the polymer, so that excess transesterifying compound does not
25 have to be removed in further processing steps.

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- 1 Esterification or transesterification can be facilitated by use of the transesterification
2 catalysts discussed above.
- 3 The reactive extruder is preferably a twin-screw intermeshing reactive extruder.
4 Uniform and intensive mixing such as that supplied by kneading blocks and right-hand
5 elements is particularly preferred. See U.S. Ser. No. 08/144,173, filed Oct. 27,
6 1993, in this regard.
- 7 A reactive extruder may be used in series with one or more reactive extruders or with
8 other processing equipment. When one reactive extruder is used, it is typically
9 divided into at least two zones, a reaction zone and a devolatilization zone. The
10 pressure in the reaction zone is typically at essentially atmospheric pressure. The
11 reaction zone may be under slight pressure due to the heat and extruder's action on
12 the polymer. The devolatilization zone is typically under vacuum to assist removing
13 volatile materials from the transesterified polymer.
- 14 When the process is used to make an oxygen-scavenging polymer, an oxygen
15 scavenging-promoting transition-metal salt may be added into the polymer during the
16 transesterification reaction. Alternatively, the transition metal salt can be
17 incorporated into the polymer component by, for instance, coating pellets of the
18 transesterified ethylene copolymer with the transition-metal salt and melt-blending the
19 pellets in an extruder, thereby incorporating into the melt blend an amount of the
20 transition-metal salt that is effective to catalyze oxygen scavenging. The method of
21 incorporating the transition-metal salt into the composition is not critical, as long as
22 the transition-metal salt is dispersed throughout the composition prior to use of the
23 composition as an oxygen scavenger. The transition-metal salt can be incorporated
24 into the composition before, during, or after transesterification.

1 Preferred polymers used in the oxygen-scavenging compositions of the present
2 invention comprise ethylene alkyl acrylate copolymers which have been reacted with
3 benzyl alcohol or benzyl amine to form an ethylene benzyl acrylate or an ethylene
4 benzyl acrylamide polymer. These polymers are typically made by transesterification
5 or transamidation as described above. A particularly preferred polymer intermediate
6 is ethylene methyl acrylate copolymer. A composition of the present invention made
7 from ethylene-methyl acrylate copolymer having 40 weight percent methyl acrylate
8 can have from about 0.33 to about 17.85 mole percent of the scavenging moieties.
9 Ethylene methyl acrylate copolymer which has 24 weight percent methyl acrylate can
10 have from about 0.33 to about 9.33 mole percent of the scavenging moieties.
11 Preferably, reacted ethylene methyl acrylate copolymer will have between about 1 and
12 10 mole percent, more preferably between about 2 and 6 mole percent, and more
13 preferably still, between about 2 and 3 mole percent of the scavenging moieties. It is
14 often desirable to have partial transesterification or transamidation, thereby leaving
15 some of the alkyl acrylate moieties unreacted, so that the polymer properties can be
16 tailored to the particular application. The physical properties of the reacted polymers
17 are similar to the physical properties of unreacted alkyl acrylate copolymer. As a
18 result, a composition of the present invention using ethylene-methyl acrylate
19 copolymer to form an ethylene benzyl acrylate or ethylene methyl acrylate benzyl
20 acrylate terpolymer is optically clear and has similar processing characteristics to
21 ethylene-methyl acrylate copolymer. Ethylene-methyl acrylate copolymer which has
22 been partially transesterified to form an ethylene methyl acrylate benzyl acrylate
23 terpolymer (about 76.6/14.4/9 wt. %, respectively) and which contains about 1000
24 ppm cobalt in the form of cobalt neodecanoate is a particularly preferred composition
25 of the present invention.

26 In another preferred embodiment, the oxygen scavenging compositions of the present
27 invention utilize a polymer prepared by reacting an ethylene alkyl acrylate copolymer,

1 or an ethylene methyl methacrylate copolymer, with a benzylic amine or alcohol of
2 Formula (VIII).

(VIII)

In Formula (VIII), X is NH₂ or OH, and R is independently selected from the group consisting of hydrogen, phenyl, alkyl radicals containing from 1 to 18 carbon atoms, alkoxy radicals having from 1 to 16 carbon atoms, amine radicals having from 1 to 6 carbon atoms, aryl radicals or substituted aryl radicals having 6 to 24 carbon atoms, aryl ether radicals or substituted aryl ether radicals having from 6 to 24 carbon atoms, and ester and amide radicals of acids having from 1 to 16 carbon atoms. X is preferably NH₂ or OH, and R is preferably methyl or methoxy, and more preferably is H. The amine is preferably benzyl amine, and the alcohol is preferably benzyl alcohol. Mixtures of benzylic alcohols and benzylic amines can also be used.

15 Among other factors, it has been found that these polymers are surprisingly good
16 oxygen scavengers when combined with a transition metal salt, such as an organic
17 cobalt salt. Moreover, the oxygen scavenging capacity and other physical properties
18 of these polymers can be readily varied by selecting the amount of alkyl acrylate in
19 the copolymer reactant and the quantity of benzylic amine or alcohol used in the
20 reaction.

When a benzylic alcohol is the reactant, an especially useful composition contains between 1 and 10 mole %, and preferably between 2 and 6 mole %, of the benzylic structure of Formula (IX).

24 (IX) —CH₂—

- 1 These polymers are also useful as adhesives or electrical insulators.
- 2 Preferred polymers are poly(ethylene - methyl acrylate - benzyl acrylate) terpolymers,
- 3 and poly (ethylene - methyl acrylate - benzyl-acrylamide) terpolymers.
- 4 It is expected that an oxygen-scavenging composition having primarily benzyl ester
- 5 radicals as the scavenging moieties will be especially useful for food applications.
- 6 The oxidation product which is freed from the polymer backbone when oxygen reacts
- 7 with the polymer is a benzoic acid which, in certain quantities, is FDA-approved for
- 8 addition to foods.
- 9 Polymers containing alkyl acrylate moieties can be partially or completely saponified
- 10 by methods well-known in the art to make ionomers. One such method is disclosed
- 11 in U.S. Ser. No. 08/144,173, filed Apr. 5, 1994, which is incorporated by reference
- 12 herein in its entirety.
- 13 Optionally, the compositions and process of this invention can include exposure of the
- 14 polymer containing the oxygen scavenging-promoting transition metal to actinic
- 15 radiation to reduce the induction period, if any, before oxygen scavenging
- 16 commences. U.S. Patent No. 5,211,875, which is incorporated by reference in its
- 17 entirety, discloses a method for initiating oxygen scavenging by exposing a film
- 18 comprising an oxidizable organic compound and a transition metal catalyst to actinic
- 19 radiation. A composition of the present invention which has a long induction period
- 20 in the absence of actinic radiation but a short or non-existent induction period after
- 21 exposure to actinic radiation is particularly preferred. Compositions which are
- 22 activated by actinic radiation can be stored without special preparation or storage
- 23 requirements, such as being packaged or kept in a nitrogen environment. They
- 24 maintain a high capability for scavenging oxygen upon activation with actinic
- 25 radiation. Thus, oxygen scavenging can be activated when desired.

1 The radiation used can be actinic, e.g., ultraviolet or visible light having a wavelength
2 of about 200 to 750 nanometers (nm), and preferably having a wavelength of about
3 200 to 400 nm. When employing this method, it is preferable to expose the
4 composition to at least 0.01 Joules per gram of composition of this invention. A
5 typical amount of exposure is in the range of 0.1 to 100 Joules per gram. Other
6 sources of radiation include ionizing radiation such as gamma, x-rays and corona
7 discharge. The duration of exposure depends on several factors including, but not
8 limited to, the amount and type of photoinitiator present, thickness of the layers to be
9 exposed, amount of any antioxidant present, and the wavelength and intensity of the
10 radiation source. Preferred compositions of the present invention do not require a
11 photoinitiator.

12 USE OF THE COMPOSITIONS OF THE PRESENT INVENTION AND
13 PRODUCTS OF THE REACTIVE EXTRUSION PROCESS

14 Polymers made by the reactive extrusion process of this invention are useful in many
15 applications, such as injection molding, blow molding, coatings, adhesives, and
16 packaging and protective films. For example, ethylene-methyl acrylate-benzyl
17 acrylate copolymer is useful as an electrical insulator or an adhesive, especially when
18 the polymer contains more than 1, and preferably more than 2, mole percent benzyl
19 acrylate.

20 Oxygen-scavenging compositions of the present invention are useful in many ways.
21 They can be processed into the form of high surface-area fibers for removing oxygen
22 which contacts the fibers. The compositions can be dispersed as small particles for
23 absorbing oxygen or can be coated onto materials such as metallic foil, polymer film,
24 metalized film, or cardboard to provide, in some embodiments, scavenging properties
25 and/or adhesive properties. The compositions are also useful in making articles such
26 as single or multi-layer rigid thick-walled plastic containers (typically, between 8 and
27 100 mils in thickness) or in making single or multi-layer flexible films. Some of the

1 compositions of the present invention are easily formed into films using well-known
2 means. These films can be used alone or in combination with other films or
3 materials.

4 The compositions of the present invention may be further combined with one or more
5 polymers, such as thermoplastic polymers which are typically used to form film layers
6 in plastic packaging articles. In the manufacture of certain packaging articles, well-
7 known thermosets can also be used as a polymeric diluent.

8 Selecting combinations of a diluent and the composition of the present invention
9 depends on the properties desired. Polymers which can be used as the diluent
10 include, but are not limited to, polyethylene, low or very low density polyethylene,
11 ultra-low density polyethylene, linear low density polyethylene, polypropylene,
12 polyvinyl chloride, and ethylene copolymers such as ethylene-vinyl acetate, ethylene-
13 alkyl acrylates or methacrylates, ethylene-acrylic acid or methacrylic acid, and
14 ethylene-arylic or metharylic acid ionomers. In rigid packaging applications,
15 polystyrene is used, and in rigid articles such as beverage containers, polyethylene
16 terephthalate (PET), is often used. See U.S. Patent No. 5,021,515. Blends of
17 different diluents may also be used. However, as indicated above, the selection of the
18 polymeric diluent largely depends on the article to be manufactured and the end use.
19 Such selection factors are well known in the art.

20 If a diluent polymer such as a thermoplastic is employed, it should further be selected
21 according to its compatibility with the composition of the present invention. In some
22 instances, the clarity, cleanliness, effectiveness as an oxygen scavenger, barrier
23 properties, mechanical properties and/or texture of the article can be adversely
24 affected by a blend containing a polymer which is incompatible with the composition
25 of the present invention.

1 One particular advantage of the compositions of the present invention where ethylene-
2 methyl acrylate copolymer is modified to form ethylene benzyl acrylate copolymer is
3 the substantial similarity of the properties of the ethylene benzyl acrylate copolymer to
4 the properties of ethylene-methyl acrylate copolymer and polyethylene. This permits
5 the inclusion of compositions of the present invention in a wide range of applications
6 where polyethylene and ethylene-methyl acrylate copolymer are used.

7 A blend of a composition of the present invention with a compatible polymer can be
8 made by dry blending or by melt-blending the polymers together at a temperature in
9 the approximate range of 50°C to 250°C. Alternative methods of blending include
10 the use of a solvent followed by evaporation. When making film layers or articles
11 from oxygen-scavenging compositions, extrusion or coextrusion, solvent casting,
12 injection molding, stretch blow molding, orientation, thermoforming, extrusion
13 coating, coating and curing, lamination or combinations thereof would typically
14 follow the blending.

15 The amounts of transition-metal salt, polymer comprising a polyethylenic backbone
16 having pendant moieties comprising benzyl radicals, and optional polymeric diluents
17 and additives vary depending on the article to be manufactured and its end use.
18 These amounts also depend on the desired scavenging capacity, the desired scavenging
19 rate, the induction period of the oxygen scavenger, and the particular materials
20 selected.

21 The compositions of the present invention have various induction periods before the
22 compositions become effective oxygen scavengers. For example, to scavenge oxygen
23 using essentially an ethylene benzyl acrylate copolymer, the composition must either
24 have its induction period reduced, such as by exposing it to ultraviolet light, or the
25 induction period must lapse. However, a composition comprising an ethylene benzyl
26 acrylate copolymer having one or more methoxy radicals substituted onto each phenyl

1 radical will have a very short induction period without exposure to actinic radiation,
2 so that the composition is effective to scavenge oxygen almost immediately. Thus,
3 the particular composition chosen for a given use will depend in part on the length of
4 time that the composition is to be stored prior to scavenging oxygen. See Example 29
5 and Figure 1.

6 Layers comprising the composition of the present invention may be in several forms.
7 They may be in the form of stock films, including "oriented" or "heat shrinkable"
8 films, which may ultimately be processed as bags, etc., or in the form of stretch-wrap
9 films. The layers may also be in the form of sheet inserts to be placed in a packaging
10 cavity. In rigid articles such as beverage containers, thermoformed trays or cups, the
11 layer may be within the container's walls. Even further, the layer may also be in the
12 form of a liner placed with or in the container's lid or cap. The layer may even be
13 coated or laminated onto any one of the articles mentioned above.

14 When using an ethylene benzyl acrylate copolymer in the composition of the present
15 invention, the composition can have sufficient tie-strength to be useful additionally as
16 a tie-layer in a multi-layer structure. Thus, separate tie layers may not be necessary
17 for binding the composition of the present invention into a multi-layer film.
18 Additionally, the composition using ethylene benzyl acrylate copolymer can have
19 sufficient hot-tack properties that a layer made from the composition of the present
20 invention will function additionally as the heat-seal layer.

21 In multilayered articles, the scavenging layer comprising the composition of the
22 present invention may be included with layers such as, but not necessarily limited to,
23 "oxygen barriers", i.e., layers of material having an oxygen transmission rate equal to
24 or less than 100 cubic centimeters-mil per square meter (cc-mil/m²) per day per
25 atmosphere pressure at room temperature, i.e., about 25°C. Typical oxygen barriers
26 comprise poly(ethylene vinyl alcohol), polyacrylonitrile, polyvinyl chloride,

1 poly(vinylidene dichloride), polyethylene terephthalate, silica, and polyamides. Metal
2 foil layers can also be employed.

3 The additional layers may also include one or more layers which are permeable to
4 oxygen. In one preferred embodiment, especially for flexible packaging for food, the
5 layers include, in order starting from the outside of the package to the innermost layer
6 of the package, (i) a structural layer to provide mechanical strength and to act as a
7 moisture barrier (e.g. high-density polyethylene), (ii) an oxygen barrier layer, (iii) a
8 layer comprising the composition of the present invention, and optionally, (iv) a
9 functional layer such as EVA. Control of the oxygen barrier property of (ii) allows a
10 means to regulate the scavenging life of the package by limiting the rate of oxygen
11 entry to the scavenging component (iii), and thus limiting the rate of consumption of
12 scavenging capacity. The functional layer in a multi-layered composition is a layer
13 which is added to perform functions which the adjacent layer cannot perform as well
14 as the functional layer. The functional layer can provide a barrier to stop or slow
15 migration of compounds contained within a composition of the present invention into
16 the package interior. These migrating compounds include additives or by-products of
17 oxygen scavenging. The functional layer may improve the heat-sealability, clarity
18 and/or resistance to blocking of the multi-layer film. Control of the oxygen
19 permeability of the functional layer also allows a means to set an upper limit on the
20 rate of oxygen scavenging for the overall structure independently of the composition
21 of the scavenging component (iii). This can serve the purpose of extending the
22 handling lifetime of films in the presence of air prior to sealing the package.

23 The multilayered articles can be prepared using coextrusion, coating and/or
24 lamination. In addition to oxygen barrier and oxygen permeable layers, further layers
25 such as tie-layers which function to bind the other layers into one film and adhesive
26 layers which make the overall film adhesive to other surfaces may be adjacent to any
27 of the layers listed above. Compositions suitable for tie-layers or adhesive layers

1 include those well known in the art, such as maleic anhydride functionalized
2 polyolefins.

3 To determine the oxygen scavenging capabilities of the invention, the rate of oxygen
4 scavenging can be calculated by measuring the time elapsed before the article depletes
5 a certain amount of oxygen from a sealed container. For instance, a film comprising
6 the scavenging component can be placed in an air-tight, sealed container of a certain
7 oxygen containing atmosphere, e.g., air which typically contains 20.9% oxygen by
8 volume. Then, over a period of time, samples of the atmosphere inside the container
9 are removed to determine the percentage of oxygen remaining.

10 When an active oxygen barrier is prepared, the scavenging rate can be as low as
11 0.1 cc oxygen per gram of composition of the present invention per day in air at
12 25°C and at 1 atmosphere pressure. However, preferable compositions of this
13 invention have rates equal to or greater than 1 cc oxygen per gram per day, thus
14 making them suitable for scavenging oxygen from within a package, as well as
15 suitable for active oxygen barrier applications. Many compositions are even capable
16 of more preferable rates equal to or greater than 5.0 cc O₂ per gram per day.

17 Generally, film layers suitable for use as an active oxygen barrier can have a
18 scavenging rate as low as 1 cc oxygen per square meter per mil per day when
19 measured in air at 25°C and 1 atmosphere pressure. Preferably, a layer of this
20 invention is capable of a scavenging rate greater than 10 cc oxygen per square meter
21 per mil per day, and more preferably has an oxygen scavenging rate equal to or
22 greater than about 25 cc oxygen per square meter per mil per day under the same
23 conditions, thus making it suitable for scavenging oxygen from within a package, as
24 well as suitable for active oxygen barrier applications. The scavenging rates of the
25 composition and layers of the present invention will change with changing temperature
26 and atmospheric conditions. The rates at room temperature, ambient humidity, and

- 1 one atmosphere pressure were measured because they best represent the conditions to
2 which the invention will be exposed in many instances.
- 3 In an active oxygen barrier application, it is preferable that the combination of oxygen
4 barriers and any oxygen scavenging activity create an overall oxygen transmission rate
5 of less than about 1.0 cubic centimeter-mil per square meter per day per atmosphere
6 pressure at 25°C. Another definition of acceptable oxygen scavenging is derived
7 from testing actual packages. In actual use, the scavenging rate requirement will
8 largely depend on the internal atmosphere of the package, the contents of the package
9 and the temperature at which it is stored. In actual use, it has been found that the
10 scavenging rate of the oxygen scavenging article or package should be sufficient to
11 establish an internal oxygen level of less than 0.1% in less than about four weeks.
- 12 In a packaging article made according to this invention, the scavenging rate will
13 depend primarily on the amount and nature of the composition of the present
14 invention in the article, and secondarily on the amount and nature of other additives
15 (e.g., diluent polymer, antioxidant, etc.) which are present in the scavenging
16 component, as well as the overall manner in which the package is fabricated, e.g.,
17 surface area/volume ratio.
- 18 The oxygen scavenging capacity of an article comprising the invention can be
19 measured by determining the amount of oxygen consumed until the article becomes
20 ineffective as a scavenger. The scavenging capacity of the package will depend
21 primarily on the amount and nature of the scavenging moieties present in the article,
22 as discussed above.
- 23 In actual use, the oxygen scavenging capacity requirement of the article will largely
24 depend on three parameters of each application:

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- 1 1. the quantity of oxygen initially present in the package,
- 2 2. the rate of oxygen entry into the package in the absence of the
- 3 scavenging property, and
- 4 3. the intended shelf life for the package.

5 The scavenging capacity of the composition can be as low as 1 cc oxygen per gram,
6 but is preferably at least 10 cc oxygen per gram, and more preferably at least 50 cc
7 oxygen per gram. When such compositions are in a layer, the layer will preferably
8 have an oxygen capacity of at least 250 cc oxygen per square meter per mil thickness
9 and more preferably at least 500 cc oxygen per square meter per mil thickness.

10 Other factors may also affect oxygen scavenging and should be considered when
11 selecting compositions. These factors include but are not limited to temperature,
12 relative humidity, and the atmospheric environment in the package.

13 As illustrated in the Examples, some embodiments of the invention go through an
14 "induction period" before they exhibit oxygen scavenging. It has been found that this
15 induction period can be shortened substantially by exposing the composition to
16 radiation. To initiate oxygen scavenging in an oxygen scavenger is defined herein as
17 facilitating scavenging such that the induction period of oxygen scavenging is
18 significantly reduced or eliminated. The induction period is the period of time before
19 the scavenging composition exhibits useful scavenging properties. Further, initiation
20 of oxygen scavenging may also apply to compositions which have an indeterminate
21 induction period in the absence of radiation.

22 While the exact manner in which oxygen scavenging is initiated is not known, it is
23 believed, without being held to any specific theory, that one or more of the following
24 occurs when the oxygen scavenger is exposed to radiation:

- 1 a. substantial depletion of any antioxidant(s), if present, thus allowing
2 oxidation to proceed;

- 3 b. activation of the transition metal catalyst through a change in the
4 metal's oxidation state and/or its configuration of ligands, thus
5 increasing its effect on scavenging; or

- 6 c. a substantial increase in free radical and/or peroxide species present in
7 the system, despite the inhibiting effect of any antioxidant(s) if present
8 or remaining.

9 When using oxygen scavenging layers or articles, exposure to radiation can be during
10 or after the layer or article is prepared. If the resulting layer or article is to be used
11 to package an oxygen sensitive product, exposure can be prior to, during, or after
12 packaging. For best uniformity of radiation, exposure should occur when the layer or
13 article is a flat sheet.

14 A composition of the present invention comprising a transition-metal salt and an
15 ethylene benzyl acrylate provides substantial advantages in packaging food products.
16 An article or wrap for containing food can be made from the composition, and
17 oxygen scavenging capabilities of the composition can be initiated by exposing the
18 article or film to actinic radiation to reduce the induction period prior to or even after
19 food is enclosed within the composition of the present invention. This provides the
20 ability to supply food having the freshest flavor. Also, initiation of the oxygen
21 scavenging properties at the time of packaging food permits the greatest shelf-life,
22 since the full oxygen scavenging capacity of the article or film is utilized in keeping
23 oxygen out of the food.

1 The compositions and methods are illustrated by the following examples, which are
2 not intended to limit the invention in any way.

Example 1

Autoclave Synthesis of Ethylene - Benzyl Acrylamide Copolymer A

One hundred (100) parts by weight of an ethylene - methyl acrylate copolymer, which contained 40 wt. % methyl acrylate (MA) and 60 wt. % ethylene, and had a melt-index (MI) of 8 g/10 min., was charged to a 300 cc autoclave with 100 parts of benzyl amine. The mixture was heated to 240°C under nitrogen for 5 hours with continued stirring. The resulting polymer was pulverized under liquid nitrogen and washed with hexane, then methanol. After drying under vacuum, 107 parts of polymer A was obtained. Infra-red spectroscopy and nitrogen analysis indicated quantitative conversion of the methyl ester to the benzyl-amide. 95 parts of nylon-6 from Custom Resin, Inc. were blended with 5 parts of Polymer A and cobalt neodecanoate in the ratio provided in Example 12 in a Haake System 90 Rheomix TW-100 conical twin-screw extruder (hereafter "Haake-90") at 210°C. Films were prepared by the method of Example 27.

Example 2

Solution Synthesis of Ethylene - 3-Methoxybenzyl-acrylamide Copolymer B

19 One hundred (100) parts by weight of an ethylene - methyl acrylate copolymer (40
20 wt. % MA) was dissolved in 150 parts of decalin at 180°C. 54 parts of 3-
21 methoxybenzyl amine was added along with 24 parts of 2-pyridone, and the solution
22 was refluxed at 184°C for 12 hours. After cooling, the polymer solution was
23 precipitated in methanol and dried in a vacuum oven to give polymer B. Infra-red
24 analysis indicated a quantitative conversion of ester to amide. Blends with nylon-6
25 from Custom Resin, Inc. were prepared by feeding 5 parts of Copolymer B and 95
26 parts of nylon-6 to a Haake-90 twin-screw extruder at 210°C. Films were prepared
27 by the method of Example 27.

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Example 3

Solution Synthesis of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer C

One hundred (100) parts by weight of an ethylene-methyl acrylate copolymer (20 wt. % MA) was dissolved in 150 parts of decalin, along with 50 parts of benzyl alcohol and 0.5 part of tetraethyl titanate, a transesterification catalyst. The mixture was refluxed at 184°C for 3 hours and worked up as described in Example 2. NMR analysis indicated 88 % conversion of methyl ester to benzyl ester.

Example 4

Solution Synthesis of Ethylene-Methyl Acrylate-Benzyl Acrylate Ternopolymer D

The procedure of Example 3 was followed except that 0.5 part of di-butyl tin dilaurate was used instead of tetraethyl titanate. Polymer D was isolated with a 72 % conversion of methyl ester to benzyl ester after 7 hours of reaction.

Example 5

Solution Synthesis of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer E

The procedure of Example 3 was followed except that 0.5 part of sodium methoxide was used instead of the tetraethyl titanate. Polymer E was isolated with a 64 % conversion of methyl ester to benzyl ester after 10 hours of reaction.

Example 6

Solution Synthesis of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer F

The procedure of Example 3 was followed except that 0.5 part of toluene sulfonic acid was used instead of the tetraethyl titanate. Polymer F was isolated with a 43 % conversion of methyl ester to benzyl ester after 15 hours of reaction.

Reactive Extrusion

Examples 7-11 were produced via reactive extrusion. In these examples, a Werner-Pfleiderer ZSK-30 twin-screw extruder was used. Ethylene-methyl acrylate

1 copolymer was fed into the extruder and melted, and the reactant(s) (such as benzyl
2 alcohol) and catalyst(s) were added to the extruder in a subsequent reaction zone.
3 Although the following examples utilized ethylene-methyl acrylate copolymer, the
4 method described herein is not limited to use of only ethylene-methyl acrylate
5 copolymer.

6 Two vent ports on the extruder produced a higher conversion of methyl ester to
7 benzyl or benzylic ester, and they reduced the flooding which often occurred in a
8 screw with only one vent port. The first vent port downstream of the point where
9 reactant(s) and catalyst(s) are added was open to the atmosphere to allow reaction by-
10 products (in the examples, methanol) to escape. The by-products may also be
11 removed under slight vacuum. The second vent port, downstream of the first, was
12 under vacuum to remove any residual reactants (such as benzyl alcohol), which
13 normally have higher boiling points than the by-products. Additional down-stream
14 vent ports can be used, if desired.

15 The temperature in the extruder was selected primarily to provide a uniform mixture
16 of melted polymer, reactant(s) and catalyst(s) without degrading the polymer.
17 However, the temperature was also selected to produce the greatest difference in
18 vapor pressure between the by-products and the reactants (where the by-products have
19 a lower boiling-point than the reactants). Normally, the temperature will be at or
20 slightly below the boiling point of the reactants.

21 In some of the following examples, ethylene-methyl acrylate copolymer and benzyl
22 alcohol were reacted at about 205°C, which is the boiling point of benzyl alcohol.
23 The first vent port pressure was about 760 mm Hg, and the second vent port pressure
24 was about 25 mm Hg. This method provided a uniform mixture of copolymer,
25 reactants, and catalyst, and also gave the greatest difference in vapor pressure
26 between benzyl alcohol and methanol. This procedure provides improved conversions

of methyl ester to benzyl ester over the method where one vent port is used to remove both the byproduct, methanol, and excess reactant, benzyl alcohol.

Example 7

Preparation of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer G by Reactive Extrusion

Ethylene - methyl acrylate copolymer (40 wt. % MA, 8 g/10 min. MI) copolymer was fed into a Werner Pfleiderer ZSK-30 twin screw extruder at a feed rate of 3 kg/hr with a barrel temperature of about 205-210°C. Benzyl alcohol and tetraethyl titanate were fed into the first mixing zone at rates of 1.5 kg/hr and 15 g/hr, respectively. The resulting polymer was pelletized, and NMR analysis indicated a 29% conversion of methyl ester to benzyl ester with no detectable amount of free benzyl alcohol. The melt index of the resulting Terpolymer G was 7.75 g/10 min at 190°C, and its composition was 54 wt. % ethylene, 26 wt. % methyl acrylate, and 20 wt. % benzyl acrylate. The polymer composition was calculated based on NMR analysis.

Example 8

Preparation of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer H by Reactive Extrusion

The procedure of Example 7 was followed, except ethylene-methyl acrylate copolymer having 24 wt. % MA and 2 g/10 min. MI was used, while the benzyl alcohol and titanium catalyst feed rates were 1.8 kg/hr and 18 g/hr, respectively. The product, polymer H, had a MI of 2.19, with a 51 % conversion of methyl ester to benzyl ester based on NMR analysis. The weight ratio of ethylene/methyl acrylate/benzyl acrylate of Polymer H was 69/10/21.

Example 9

Preparation of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer H-Me, Having a Partial 3-methyl Substitution on the Phenyl Ring

The procedure of Example 8 was followed to make Polymer H-Me, except that a solution of 99 wt. % benzyl alcohol and 1 wt. % of 3-methylbenzyl alcohol was used in place of the benzyl alcohol of Example 8. 48 % of the methyl ester radicals were converted to benzyl ester radicals or 3-methylbenzyl ester radicals, based on NMR analysis. The weight ratios of ethylene/methyl acrylate/benzyl acrylate were 69/11/20.

Example 10

Preparation of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer H-OMe, Having a Partial 3-methoxy Substitution on the Phenyl Ring

The procedure of Example 9 was followed to make Polymer H-OMe, except 3-methoxybenzyl alcohol was substituted in place of the 3-methylbenzyl alcohol of Example 9. 45 % of the methyl ester radicals were converted to benzyl ester radicals or 3-methoxybenzyl ester radicals. The weight ratios of ethylene/methyl acrylate/benzyl acrylate were 69/12/19 for Polymer H-OMe.

Example 11

Preparation of Ethylene-Methyl Acrylate-Benzyl Acrylate Terpolymer I by Reactive Extrusion

The procedure of Example 7 was followed except that a 20 % MA ethylene-methyl acrylate copolymer and a MI of 6 g/10 min. was used as the feed polymer. The product, polymer I, had a melt index of 6.25 g/10 min, with a 39 % conversion of methyl ester radicals to benzyl ester radicals, based on NMR analysis. The weight ratio of ethylene/methyl acrylate/benzyl acrylate was 75/11/14.

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Example 12

Blending of Cobalt Salt with Polymer A

3 1000 parts of polymer A pellets were tumble mixed with 8.3 parts of cobalt
4 neodecanoate (which contains 1 part cobalt) in 20 parts of hexane. The hexane was
5 removed by vacuum, and the cobalt-coated resins were extruded into pellet form, then
6 into films by the method of Example 27.

Example 13

Blending of Cobalt Salt with Polymer B

9 The method of Example 12 was repeated, substituting Polymer B for Polymer A.

Example 14

Blending of Cobalt Salt with Polymer C

12 The method of Example 12 was repeated, substituting Polymer C for Polymer A.

13 The film made from this polymer had the following properties: tensile strength 1243
14 psi; elongation 726%; and melting point 86°C.

Analyses for tensile strength, elongation, Young's modulus, and 1 % secant were performed by ASTM method no. D-882.

Example 15

Blending of Cobalt Salt with Polymer D

19 The method of Example 12 was repeated, substituting Polymer D for Polymer A.

Example 16

Blending of Cobalt Salt with Polymer E

22 The method of Example 12 was repeated, substituting Polymer E for Polymer A.

Example 17

Blending of Cobalt Salt with Polymer F

3 The method of Example 12 was repeated, substituting Polymer F for Polymer A.

Example 18

Blending of Cobalt Salt with Polymer G

6 The method of Example 12 was repeated, substituting Polymer G for Polymer A.

Example 19

Blending of Cobalt Salt with Polymer H to Form Polymer H-1000

9 The method of Example 12 was repeated, substituting Polymer H for Polymer A.

Example 20

Blending of Cobalt Salt with Polymer H to Form Polymer H-250

12 The method of Example 19 was repeated, using 2.1 parts of cobalt neodecanoate
13 (which contains 0.25 part cobalt) in 5 parts of hexane in place of the 8.3 parts of
14 cobalt neodecanoate in 20 parts of hexane.

Example 21

Blending of Cobalt Salt with Polymer H to Form Polymer H-500

17 The method of Example 19 was repeated, using 4.2 parts of cobalt neodecanoate
18 (which contains 0.50 part cobalt) in 10 parts of hexane in place of the 8.3 parts of
19 cobalt neodecanoate in 20 parts of hexane.

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Example 22

Blending of Cobalt Salt with Polymer H to Form Polymer H-2000

The method of Example 19 was repeated, using 16.6 parts of cobalt neodecanoate (which contains 2.0 parts cobalt) in 40 parts of hexane in place of the 8.3 parts of cobalt neodecanoate in 20 parts of hexane.

Example 23

Blending of Cobalt Salt with Polymer H-Me

The method of Example 12 was repeated, substituting Polymer H-Me for Polymer A.

Example 24

Blending of Cobalt Salt with Polymer H-OMe

The method of Example 12 was repeated, substituting Polymer H-OMe for Polymer A.

Example 25

Blending of Cobalt Salt with Polymer I

The method of Example 12 was repeated, substituting Polymer I for Polymer A.

Example 26

Melt Blending of Cobalt Salt to Copolymers

Polymers A to I are individually melt processed at about 180°C in a ZSK-30 twin screw extruder. The polymer feed rate is maintained at 10 kg/hr while cobalt neodecanoate is metered into the first mixing zone at a rate of 83 g/hr. The products which contain about 1000 ppm Co are pelletized and are stored for later film processing.

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Example 27

Polymer Film Preparation with Randcastle Extruder

A Randcastle Microtruder was used to extrude mono-layer films of about 5 mil thickness of polymers with cobalt. The die temperature, feed block, and adapter were set at 420°F, and the feeder RPM was set at 143. All films were soft and flexible and were observed to have good clarity.

Example 28

UV Initiation of Oxygen Scavenging

Some films were irradiated prior to performing oxygen scavenging studies. These films were exposed to UV radiation under a 15 watt UV lamp (a Blak-Ray lamp, model XX-15S, made by UVP Inc.) for 5 minutes at a distance of 5 inches.

The effect of UV irradiation is clearly seen for Polymer H-1000 of Example 19, for example. The irradiated film scavenged oxygen much more rapidly.

Example 29

Oxygen Scavenging without UV Irradiation

2 grams of film of each polymer from Examples 19, 23, and 24 were sealed in separate 1-liter capacity bottles, and oxygen depletion was monitored using a Mocon 710 oxygen analyzer.

The results shown in Figure 1 show that these samples scavenge oxygen without UV irradiation at different rates, depending on the group substituted onto the phenyl ring.

Example 30

Oxygen Scavenging Rate and Capacity Studies

Rate and capacity of oxygen removal at 25°C and at 55°C were measured by placing polymer film samples in sealed bottles which had 20.9% or 2% oxygen, as specified.

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1 and monitoring the oxygen depletion by gas chromatography and/or by Mocon 710
2 oxygen analyzer.

3 About 5 grams of polymer film were used for 22 cc and 250 cc capacity bottles.
4 About 2 grams of polymer film were used for 1 liter capacity bottles. Oxygen
5 depletion was monitored by gas chromatography (GC) or with a Mocon 710 oxygen
6 analyzer. The following Table 1 exemplifies the oxygen scavenging activities
7 recorded for 22 cc, 250 cc and 1 liter bottles.

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				UV IRRADIATED	4 hr. ⁴	1 day ⁴	2 days ⁴	4 days ⁴	7 days ⁴	14 days ⁴	21 days ⁴
1	COMPOSITION # ¹	BOTTLE OF EXAMPLE # ¹	SIZE (cc) ²								
2				no							
3					20.9						
4						20.9					
5	12	22	no								
6	12 ³	22	no								
7	13	22	no								
8	14	22	no								
9	18	22	yes								
10	19	1000	no								
11	19	1000	yes								
12	20	1000	no								
13	20	1000	yes								
14	21	1000	no								
15	21	1000	yes								
16	22	1000	no								
17	22	1000	yes								
18	23	250	no								
19	23	250	yes								

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1	24	250	no	20.2	20.7	20.5	0.3
2	24	250	yes	20.2	7.7	0.0	
3	25	250	no	18.6	0.5		
4	34	1000	no	20.7	20.4	20.4	20.0
5	34	1000	yes	20.7	20.4	20.2	20.0
6	38	1000	yes	20.9	20.8	20.1	20.7

7 NOTES:

- 8 1. Oxygen-scavenging temperature was 25°C, except where noted otherwise.
- 9 2. All bottles in these experiments had 20.9 % oxygen when the samples were placed
10 in the bottles.
- 11 3. Oxygen-scavenging temperature for this experiment was 55°C.
- 12 4. Times listed are lengths of time after the samples were placed in bottles to
13 scavenge oxygen.
- 14 Numbers in these columns are percent oxygen remaining in the bottles.

Example 31

Oxygen Scavenging Capacity Studies

The total oxygen absorption capacity per gram of film of the polymer of Example 19 (Polymer H-1000) was measured and is shown in Figure 2. Also, the capacity of polymer H-1000 to scavenge oxygen within the first few days at reduced oxygen concentration (i.e. starting at 2 % O₂) was measured and compared with a commercial oxygen scavenger, Ageless, available from Mitsubishi Gas Chemical Co. (see Figure 3). These conditions simulate a method of purging oxygen with nitrogen gas during packaging of food. Figure 3 shows that polymer H-1000 was superior to Ageless in scavenging oxygen at low concentrations, since polymer H-1000 scavenged all but 0.02 % of the oxygen from the container head-space while Ageless left 0.12 % of the oxygen.

Example 32

Effect of Cobalt Level on Oxygen Scavenging Rates and Capacities

15 The cobalt content of compositions using Polymer H was varied to determine its
16 effect on the oxygen scavenging rate. Oxygen scavenging rates and capacities were
17 measured for UV-irradiated films of polymers from Examples 19 through 22, and the
18 results are shown in Figure 4.

Example 33

Improved Barrier Properties

Polymer of Example 25 was co-extruded with a commercial oxygen barrier ethylene vinyl alcohol (EVOH) (available from Eval Co. of America, grade Eval F-104) and a Bynel 388 tie layer (available from DuPont), using a Randcastle Minitruder. The resulting 3-layer structures showed a four-fold reduction in oxygen transmission rate over EVOH alone. Similar results were observed for 3-layer structures made with polymer H-1000 of Example 19. See Figure 5.

Comparative Example 34

Oxygen Scavenging Performance of Ethylene - Methyl Acrylate Copolymer with Cobalt

Ethylene - methyl acrylate copolymer (EMAC® copolymer grade SP-2260, made by Chevron) having 24 wt. % MA and a MI of 2 g/10 min. was blended with 1000 ppm cobalt as described in Example 12. The resin containing cobalt salt was extruded into a film as described in Example 27. The films were tested with and without the UV radiation as described in Example 28. Little oxygen scavenging was found in either case.

Example 35

Analysis of Products of Oxidation

After Polymer H-1000 was oxidized for six days using a 5 g. sample in a bottle having a capacity of 1000 cc, it was extracted with methanol, concentrated, and analyzed by gas chromatography and gas chromatography coupled with mass spectroscopy. Over 95 % of the oxidation product was benzoic acid.

Physical properties of Polymer H-1000 were analyzed before and after scavenging 40.6 cc of oxygen per gram of Polymer H-1000 over a 6-day period. These results are summarized in Table 2.

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		Table 2	
		BEFORE OXIDATION	AFTER OXIDATION
1	Tensile strength (psi)	1769	712
2	% elongation	707	493
3	Young's modulus (psi)	2768	2947
4	1 % secant (psi)	2320	2463

Example 36

Synthesis of Benzylimide-containing Terpolymer from Ethylene-Butylacrylate-Maleic

Anhydride Terpolymer

11 100 parts of Lotador 4700, available from Elf Atochem, containing 3% maleic
12 anhydride, and 10 parts of 3-methoxy benzylamine are kneaded at 150°C in 50 parts
13 of decalin for 3 hours, followed by 2 hours at 185°C under vacuum to dehydrate the
14 acid-amide. Product formation can be monitored by the conversion of the anhydride
15 band to the imide band with infrared spectrometry. Precipitation of the polymer
16 solution in methanol is followed by filtration and vacuum drying overnight to produce
17 a polymer product in which there is partial conversion of the anhydride to imide.
18 1000 ppm cobalt is incorporated in this polymer, as discussed above. A thin film of
19 this polymer is extruded with the Randcastle Microtruder.

Example 37

Synthesis of Ethylene - 3-methylphenyl acrylate

100 parts of EMAC® copolymer SP-2260 (available from Chevron Chemical Co.), 16 parts of meta-methylphenol, and 0.5 part of tetraethyl titanate were refluxed in decalin at 180°C for 6 hours. The polymer product was precipitated in methanol to give polymer with 36 % of the methyl ester radicals converted to 3-methylphenyl ester radicals. Cobalt neodecanoate was added by the method of Example 12, where the

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ethylene - 3-methylphenyl acrylate replaced polymer A, and a film was made by the method of Example 27. This composition scavenged oxygen slowly.

Comparative Example 38

Poly(styrene as an Oxygen Scavenger)

A solution of approximately 20 wt. % cobalt neodecanoate in hexane was dispersed at room temperature over pellets of Chevron Grade EA3000 polystyrene (not rubber modified) in a quantity sufficient to provide about 1000 ppm by weight of cobalt in the final composition. The solvent was stripped off by use of a rotary vacuum evaporator. A film was made by the method of Example 27. The oxygen scavenging performance was determined by the method of Example 30 and is summarized in Table 1. This example shows that a benzyl radical pendant to the ethylenic backbone is much more effective in scavenging oxygen than an aryl radical such as phenyl, despite both compositions having tertiary hydrogen atoms present in the polymer backbone.

Example 39

Poly(Methyl Methacrylate-Benzyl Methacrylate)

17 350 grams (3.5 mole) of polymethylmethacrylate (Plexiglass VO 44 from Rohm &
18 Haas), 378 grams of benzyl alcohol (3.5 mole) and 0.54 gram (0.1 mole %) of an
19 antioxidant Irganox 1076 were heated to 180°C to dissolve them in 550 cc of decalin.
20 13.86 grams of tetraisopropyl titanate was added and the temperature was maintained
21 at 180-190°C for 14 hours, and during this time 23 ml of distillate containing
22 methanol was collected and the reaction was stopped. The polymer was precipitated
23 in methanol then washed with hexane. After drying at 55°C overnight in an vacuum
24 oven, 404 gram of polymer were recovered with a DSC melting point of 93-94°C.
25 NMR analysis showed a 22.6 % conversion of methyl ester to benzyl ester.

1 This polymer was blended with cobalt neodecanoate by the method of example 12,
2 and film was prepared as in example 27. The film was UV-irradiated as discussed
3 above. This film scavenged about 10 cc of oxygen/gram of polymer after about 25
4 days at 25°C.

Example 40

Synthesis of poly(ethylene-vinyl acetate-phenyl acetate)

7 3 kg/hr. of ethylene-vinyl acetate copolymer (33% vinyl acetate) and 0.5 wt. %
8 Irganox 1076 are fed to the reactive extruder, which has a barrel temperature of
9 225°C. 0.5 kg/hr. of a solution containing 80% phenyl acetic acid and 0.2 wt. %
10 toluene sulfonic acid in xylene is fed to the first mixing zone. The resulting polymer
11 is pelletized, dissolved, precipitated in methanol, and dried under vacuum. This
12 polymer is compounded with transition metal salt as described in Example 12.

Example 41

Synthesis of dibenzyl 1,10-decanecarboxylate

230 grams of 1,10-decanedicarboxylic acid, 238 grams of benzyl alcohol and 0.5 gram of toluene sulfonic acid were dissolved in 200 ml of toluene and brought to 105°C with stirring. The mixture was kept at this temperature for 10 hours, and 2 moles of water were slowly distilled off. Extra benzyl alcohol and toluene were removed by vacuum. Yield was 454 grams. The structure was confirmed by NMR.

1 WHAT IS CLAIMED IS:

- 2 1. A composition comprising a transition-metal salt and a component which has
3 an ethylenic backbone and a pendant and/or terminal moiety comprising a
4 benzyl radical, wherein the composition is effective to scavenge at least 1 cc of
5 oxygen per gram of said composition.
- 6 2. The composition of Claim 1 further comprising a heteroatom-containing
7 radical directly bonded to said benzyl radical.
- 8 3. The composition of Claim 2 wherein said benzyl radicals comprise benzyl
9 radicals substituted with at least one radical selected from the group consisting
10 of hydrogen, alkyl radicals containing from 1 to 18 carbon atoms, alkoxy
11 radicals having from 1 to 16 carbon atoms, amine radicals having from 1 to 6
12 carbon atoms, ester and amide radicals of acids having from 1 to 16 carbon
13 atoms, aryl radicals or substituted aryl radicals having 6 to 24 carbon atoms,
14 and aryl ether radicals or substituted aryl ether radicals having from 6 to 24
15 carbon atoms.
- 16 4. The composition of Claim 3 wherein said benzyl radicals comprise benzyl
17 radicals having the phenyl substituted with at least one radical selected from
18 the group consisting of hydrogen, alkyl radicals containing from 1 to 6 carbon
19 atoms, alkoxy radicals having from 1 to 6 carbon atoms, amine radicals having
20 from 1 to 6 carbon atoms, ester and amide radicals of acids having from 1 to 6
21 carbon atoms, aryl radicals or substituted aryl radicals having 6 to 15 carbon
22 atoms, and aryl ether radicals or substituted aryl ether radicals having from 6
23 to 15 carbon atoms.

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- 1 33. A multi-layer composition comprising:
 - 2 A) a first layer comprising an oxygen barrier layer; and
 - 3 B) a second layer comprising the composition of Claim 24.
- 4 34. The composition of Claim 33 further comprising a third layer comprising a
5 functional layer.
- 6 35. The composition of Claim 33 further comprising a third layer comprising a
7 structural layer.
- 8 36. The composition of Claim 35 further comprising a fourth layer comprising a
9 functional layer.
- 10 37. A rigid thick-walled composition comprising the composition of Claim 1.
- 11 38. A process comprising:
 - 12 A. forming a melt of a polymer having a polyethylenic backbone and
13 pendant ester moieties; and
 - 14 B. contacting the melt with a transesterifying compound in a reactive
15 extruder under transesterification conditions, where the polymer
16 undergoes transesterification but not alcoholysis, and the polymer after
17 transesterification has a polyethylenic backbone and pendant ester
18 moieties.
- 19 39. The process of claim 38 further comprising contacting the melt with a
20 transesterification catalyst in the reactive extruder.
- 21 40. The process of claim 38 wherein the reaction occurs essentially at atmospheric
22 pressure.

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- 1 41. The process of claim 38 further comprising adding an amount of transition
2 metal salt that is effective to promote oxygen scavenging in the transesterified
3 polymer.
- 4 42. The process of claim 41 wherein the transition metal salt comprises a cobalt
5 metal salt.
- 6 43. The process of claim 41 further comprising irradiating the transesterified
7 polymer with actinic radiation.
- 8 44. The process of claim 38 wherein the polymer comprises ethylene alkyl acrylate
9 copolymer or ethylene alkyl acrylate copolymer grafted with maleic anhydride.
- 10 45. The process of claim 44 wherein the polymer comprises ethylene methyl
11 acrylate copolymer.
- 12 46. The process of claim 44 wherein the transesterifying compound comprises
13 benzyl alcohol.
- 14 47. The process of claim 45 wherein the transesterifying compound comprises
15 benzyl alcohol.
- 16 48. The process of claim 47 further comprising adding an amount of transition
17 metal salt that is effective to promote oxygen scavenging in the transesterified
18 polymer.
- 19 49. The process of claim 48 further comprising irradiating the transesterified
20 polymer with actinic radiation.

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- 1 50. The process of claim 44 wherein the transesterifying compound comprises
- 2 3-methylbenzyl alcohol.
- 3 51. The process of claim 44 wherein the transesterifying compound comprises
- 4 3-methoxybenzyl alcohol.
- 5 52. The process of claim 38 wherein the polymer comprises an ethylene vinyl
- 6 acetate copolymer.
- 7 53. The process of claim 52 wherein the transesterifying compound comprises
- 8 phenyl acetic acid.

Figure 1

EFFECT OF BENZYL ALCOHOL(BZA) SUBSTITUTION OXYGEN SCAVENGING RATE

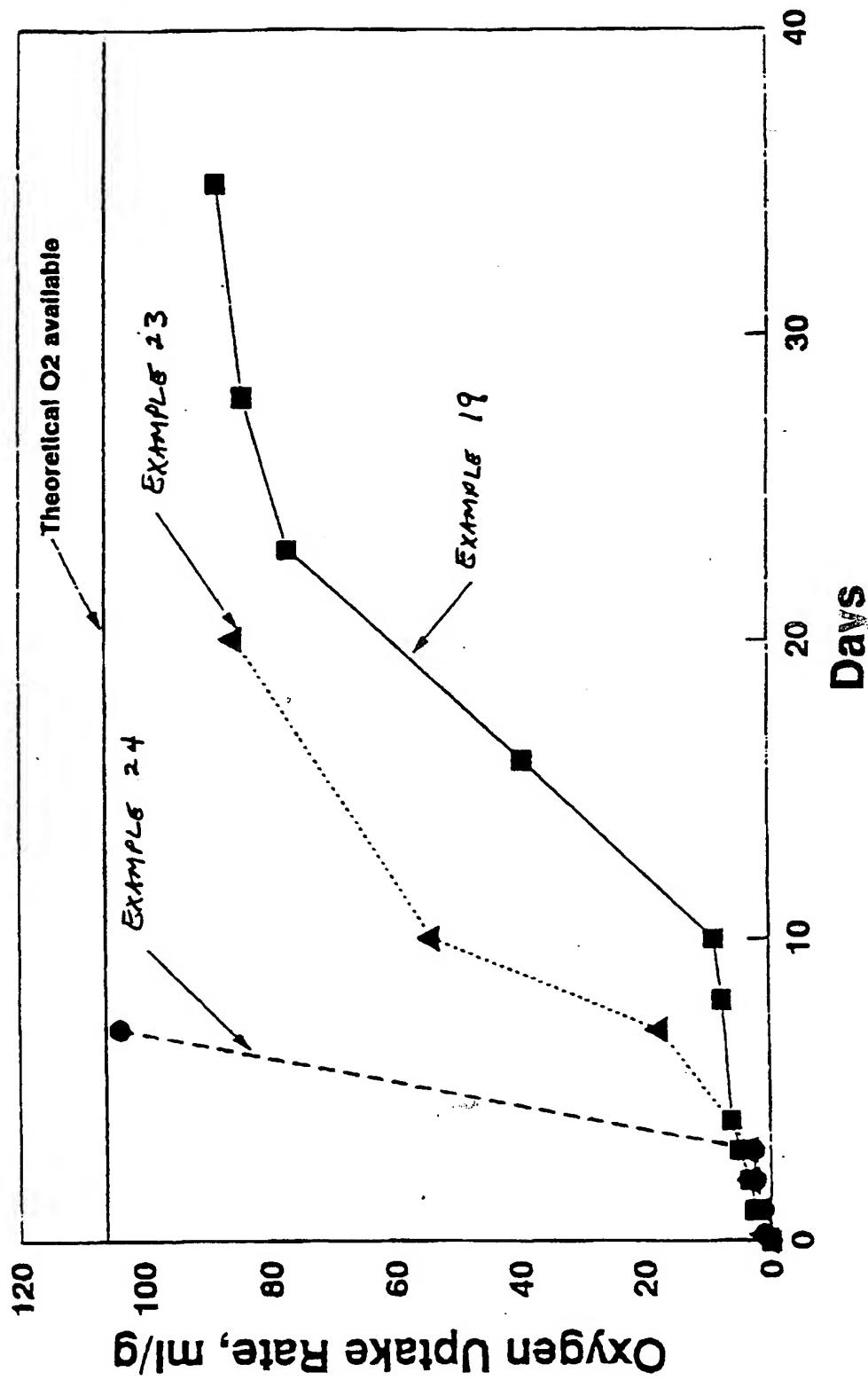


FIGURE 2
Oxygen Scavenging Capacity

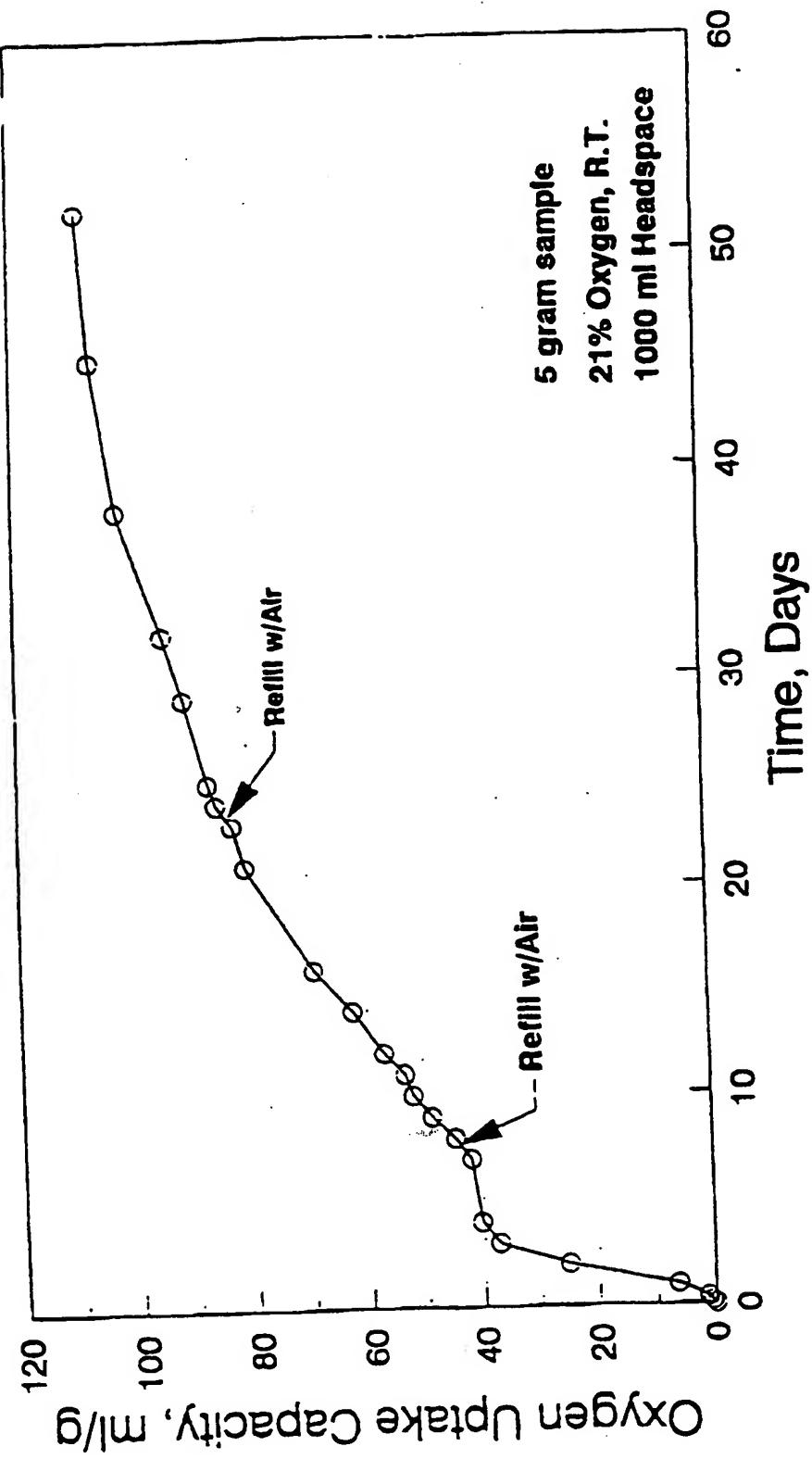


Figure 3

Oxygen Scavenging Rate Effect of Modified Atmosphere

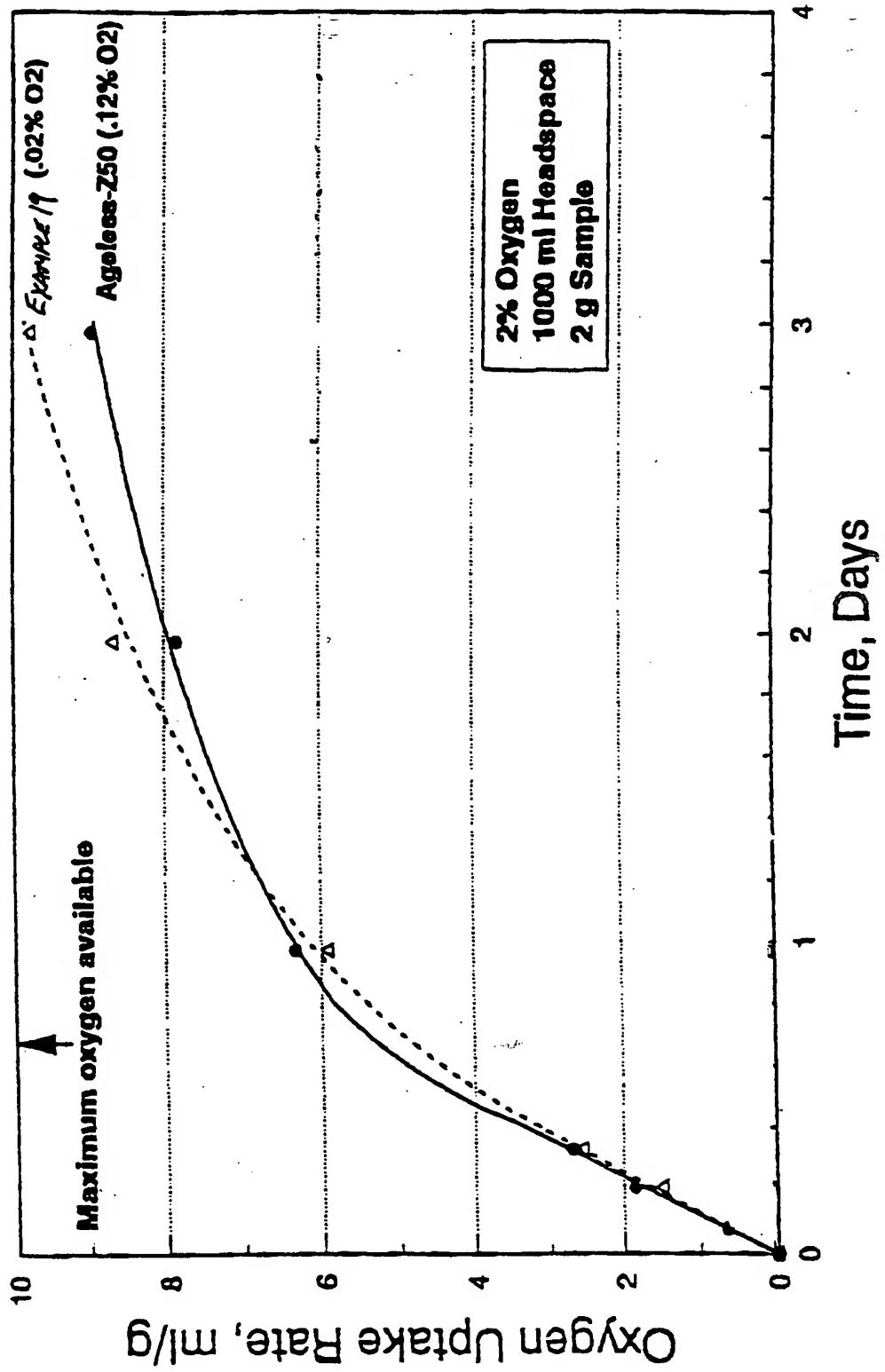


Figure 4
OXYGEN SCAVENGING RATE
Effect of Cobalt Concentration

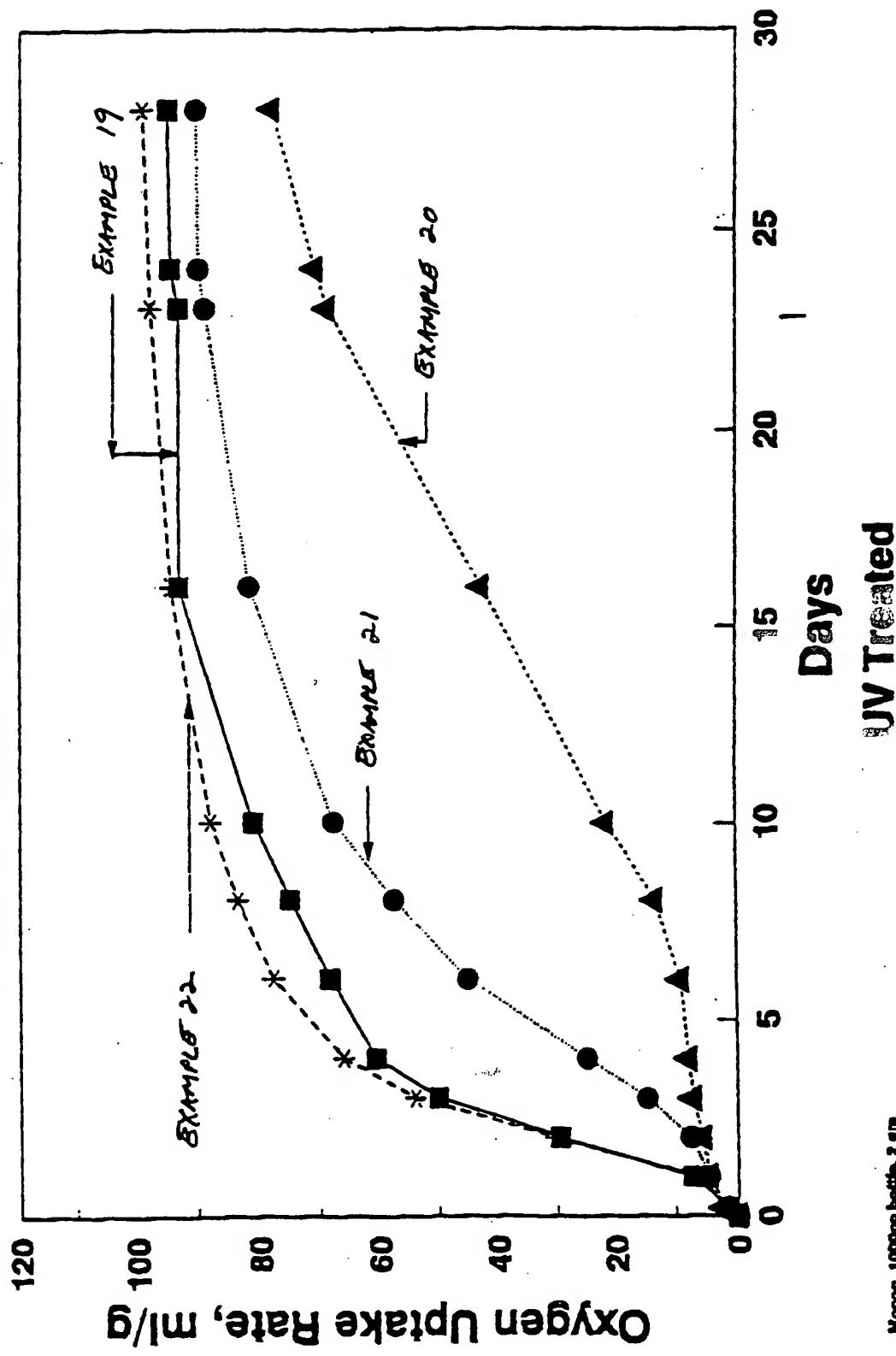


Figure 5

Oxygen Transmission Rate (OTR)

Effect of UV Irradiation of Multi-Layer Film

